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NOTES

ON THE

CHEMICAL LECTURES

FOR

FIRST-YEAR STUDENTS

IN THE

MEDICAL DEPARTMENT OF THE UNIVERSITY
OF PENNSYLVANIA.

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THE following notes, by Dr. Marshall, of my Lectures on Chemistry, for students, have been published with my consent and authority.

THEODORE G. WORMLEY

TRANSFER FROM C. G. NOV 1934

NOTES

ON

CHEMICAL LECTURES.

GENERAL PROPERTIES OF MATTER.

CHEMICAL PHYSICS.

Physics is the study of matter under all its various phases.

Physics or Natural Science may be divided into the following branches:—

- Physics or Natural Science.
  - Natural History.
    - Inorganic.
      - Mineralogy.
      - Geology.
    - Organic.
      - Botany.
      - Zoölogy.
  - General Philosophy.
    - Natural Philosophy.
    - Chemistry.
    - Astronomy.

Chemistry is that branch of physics, or the science, which treats of the properties and laws relating to the ultimate molecules and atoms of matter.

Science is the knowledge of the laws pertaining to any given class of phenomena.

Chemistry became a fixed science in 1774, when oxygen was discovered.

Properties of matter: Physical and chemical.

A law in physics expresses what will take place when certain conditions are supplied—as the law of gravity.

A **molecule** is the smallest quantity of matter that can exist in the free state. It is the smallest particle of matter into which a body can be divided without losing its identity.

Example: The smallest particles of sodium chloride which can exhibit the properties of this substance are molecules.

Molecules are made up of atoms. Atoms enter into combination to form molecules.

In **elementary matter** the molecules are composed of atoms of matter of the same kind.

In **compound matter** the molecules consist of dissimilar atoms.

All matter, either simple or in combination, is made up of about 70 elementary forms of matter.

Oxygen is an elementary form of matter.

An **atom** is the smallest particle of matter that can enter into chemical combination. It is that quantity by weight of matter which is constant in regard to its capacity for heat.

A mass of oxygen is made up of molecules; the molecules are made up of atoms.

Hydrogen is an elementary form of matter. An atom of hydrogen may combine with another atom of hydrogen and form a molecule.

An *atom* of hydrogen may combine with *one atom* of chlorine, forming a molecule of hydrochloric acid.

The atom of hydrogen does not exceed the $\frac{1}{500000000}$ of an inch in its largest diameter.

The elementary forms of matter unite among themselves in different proportions.

Examples:

H_2O = one molecule of water.

H_2O_2 = one molecule of hydrogen peroxide.

C_2H_6O = one molecule of alcohol.

$5C_2H_6O$ = five molecules of a definite compound made up of three of the 70 elementary forms of matter in definite proportions by weight.

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Alcohol has never been observed in the solid state.

Carbon has never been observed except in the solid state.

Matter in the gaseous state cannot be reduced to the liquid state until the matter has been brought below a certain temperature, called the **critical point.**

Carbon monoxide at ordinary temperature, under a pressure of 2790 atmospheres remains a gas; but at —139° C. and a pressure of 35.5 atmospheres it becomes a liquid; and at —210° C. it liquefies without external pressure.

3. **IMPENETRABILITY:** Two bodies cannot occupy the same space at the same time.

4. **DIVISIBILITY:** Matter may be divided indefinitely without destroying its properties.

Examples: A globule of mercury measuring $\frac{1}{25000}$ of an inch in diameter may be easily recognized by its peculiar properties, although weighing only $\frac{1}{8695000000}$ of a grain.

Newton found the opaque part of a soap bubble (essentially consisting of water) to be $\frac{1}{2500000}$ of an inch in thickness.

5. **POROSITY:** The ultimate molecules of matter are not in absolute contact.

(*a*) **Solids:** Mercury may pass through the pores of wood.

(*b*) **Liquids:** Alcohol and water when mixed occupy less space than the two when unmixed.

(*c*) **Gases:** A globe filled with vapor of water (steam) at 212° F. may have introduced into it as much vapor of alcohol as if no vapor of water were present (and in addition, as much vapor of ether may be introduced into the same globe as if no vapors of water and alcohol were present). Ten to twelve different vapors may successively be introduced into the same globe.

6. **COMPRESSIBILITY:** By external force the ultimate particles of matter may be brought more closely in contact, the molecules themselves not being in absolute contact.

Examples. (*a*) **Solids:** Compression of rubber, the compression of iron, lead, etc., by hammering.

Expansibility: Gases expand on lessening the atmospheric pressure. There is no limit to the expansibility of gases. The expansibility of gases may be illustrated by the air pump, which is an apparatus used to withdraw air from a closed vessel.

A **barometer** is an instrument used for ascertaining the atmospheric pressure. The simplest form of a barometer may be made by using a straight tube about 85 centimetres long, closed at one end, filled with mercury, and the open end closed with the thumb, then inverted over mercury and the thumb withdrawn. The mercury in the tube will sink until t equipoises the atmospheric pressure. The empty space above the mercury in the tube is called a **Torricellian vacuum.**

The atmospheric pressure at the level of the sea is taken as unity, and is assumed to be equivalent to a column of mercury 30 inches in height (equal to 762 millimetres). In the French system the atmospheric pressure at the sea level is assumed to be equivalent to a column of mercury 760 millimetres in height (equal to 29.992 inches).

The column of mercury in a barometer containing a few drops of water, at the level of the sea, will stand at a height of 758 millimetres.

Containing a few drops of alcohol, 749 millimetres.

Containing a few drops of ether, 730 millimetres.

This is due to the tension of the vapor of these liquids. The vapor tension varies with each liquid, and the greater the temperature the greater the tension.

The siphon barometer of Bunsen is the one usually employed in scientific investigations. The readings are made at the upper and lower levels of the mercury in the tube, and the sum of the two readings is the barometric pressure.

A sudden change in the barometer indicates a change in the weather. A rapid fall of mercury usually indicates a storm; a rising column indicates clearing weather.

The heights of mountains may be measured approximately by means of the barometer. The fall of one inch in the height of the column of mercury in the barometer, in ascending from the level of the sea, is equal to an altitude of 872

feet. This latter number, however, is not constant as the fall of each inch above one inch in the height of the column of mercury is not exactly equal to an altitude of 872 feet.

The volume of a gas is affected not only by pressure, but also by temperature.

All gases when heated expand $\frac{1}{273}$ or $\frac{11}{3000}$ of their volume, for each rise of 1 degree centigrade above 0° C., or $\frac{1}{490}$ of the volume for each rise of 1 degree above 32° F.

1. **Calculation to reduce the volume of a gas to 760 millimetres pressure and 0° C. temperature.**

Example: What volume will 20 cubic centimetres ot nitrogen measured at 750 millimetres pressure and 15° C. temperature occupy at 760 millimetres pressure and 0° C. temperature?

$$760 : 750 :: 20 : 19.73 \text{ c.c.} = \text{vol. at 760 millimetres;}$$

and

(273 + 15 = 288)

$$288 : 273 :: 19.73 : 18.7 \text{ c.c., vol. at 760 millimetres and } 0^\circ \text{ C. temperature.}$$

2. **Calculation:** What volume will 7.4 c.c. nitrogen at 754 millimetres and 20° C. temperature occupy at 760 millimetres and 0° C.?

$$V' = \frac{V \times (B - T)}{760 \times (1 + 0.003665\, t^\circ)}.$$

In the above formula

V' = the corrected volume.

V = observed volume.

B = observed barometric pressure.

T = tension of aqueous vapor for temperature t°.

t° = the observed temperature.

0.003665 = coefficient of expansion ot gases for each degree Centigrade.

$$\frac{7.4 \times (754 - 17.4)}{760 \times 1.073} = \frac{5450.84}{815.48} = 6.68 \text{ c.c.}$$

17.4 millimetres is the tension of aqueous vapor at 20° C. temperature. Tables in books give the tension of aqueous vapor for different degrees Centigrade.

8. **DILATABILITY** refers to the expansion of a body upon the application of heat. All matter, except when under peculiar conditions, expands on the application of heat.

(*a*) **Solids:** No two solids expand equally.

(*b*) **Liquids:** No two liquids expand equally.

(*c*) **Gases:** All gases (simple or compound) expand equally on the application of equal increments of heat.

All gases expand $\frac{1}{273}$ or $\frac{11}{3000}$ of their volume for each degree Centigrade above 0° C., or $\frac{1}{490}$ for each degree Fahrenheit above 32° F.

273	c.c.	of a gas	at 0° C.,	will become	274	c.c.	at	1° C.
273	"	"	"	"	275	"	"	2° C.
273	"	"	"	"	276	"	"	3° C.
273	"	"	"	"	288	"	"	15° C.
or,								
3000	"	"	"	"	3011	"	"	1° C.
3000	"	"	"	"	3033	"	"	3° C.
3000	"	"	"	"	3110	"	"	10° C.

9. **INERTIA:** Matter has in itself no power to change its motion or rest.

10. **INDESTRUCTIBILITY:** Matter cannot be destroyed.

Force: Force is any agent which can produce, change or destroy motion; or it is any agent which produces or tends to produce motion, or which resists any change in the relation of the ultimate molecules and atoms of matter.

The following four forms of force may be considered in this connection:—

1. Gravity.
2. Attraction of aggregation (cohesion).
3. Heterogeneous attraction (adhesion).
4. Chemical force.

1. FORCE OF GRAVITY.

Force of Gravity is the attraction possessed by every mass of matter for every other mass. It is proportionate to the

quantity of matter present in the mass, and varies inversely as the square of the distance between the attracting bodies.

A body on the surface of the earth is drawn toward the centre of the earth, at which point a body would be stationary.

As the polar diameter of the earth is about 26 miles less than its equatorial diameter, 194 pounds of matter at the equator would weigh 195 pounds at the poles.

Force of gravity cannot be annihilated. It may, however, be overcome by another force.

The act of weighing substances is a practical application of the force of gravity.

There are four systems of weights :—

Troy, Apothecaries', Avoirdupois and **Metric.**

The **metric system** is now universally employed in scientific investigations.

The **metre** is, approximately, the ten-millionth part of the distance from the Equator to the North Pole.

Length.

1 Metre = 10 decimetres = 39.37 + inches.
1 Decimetre = 10 centimetres = 3.937 inches.
1 Centimetre = 10 millimetres = 0.3937 inch.

Volume.

1 **Litre** = 1000 cubic centimetres = 1.761 pint = 35.2154 fld. oz., Imperial measure.

1 cubic centimetre = 1000 cubic millimetres = 0.0352 fld. oz., Imperial measure.

Weight.

The **gramme** is theoretically the weight of 1 c.c. of distilled water at 4° C. and 760 millimetres barometric pressure.

1 Kilogramme = 1000 grammes = 2.2054 lbs. avoir.
1 Gramme = 10 decigrammes = 15.4324 grains.
1 Decigramme = 10 centigrammes = 1.54324 grain.
1 Centigramme = 10 milligrammes = 0.154324 grain.

Specific gravity is the weight of a given volume of matter, compared with the weight of an equal volume of some other matter taken as unity.

Hydrogen is the lightest substance known; hammered iridium the heaviest. A cubic inch of hammered iridium contains about 240,000 times more matter than an equal volume of hydrogen, and would weigh about 240,000 times more than a cubic inch of hydrogen.

The **heaviest solid**, hammered iridium, is 92 times heavier than the same volume of cork, the **lightest solid** known.

The **heaviest liquid,** mercury, is 23 times heavier than the same volume of cymogen, a petroleum product, the **lightest liquid** known.

The **heaviest gas,** aluminium iodide (Al_2I_6), is 406.6 times heavier than the same volume of hydrogen, the **lightest gas** known.

The **standard for solids and liquids** is pure water, according to the **English** system, at a temperature of 62° F. and barometric pressure of 30 inches, or, according to the **French** system, at 4° C. and 760 millimetres, barometric pressure. Water has its greatest density at 4° C.

The **common standard for gases,** according to the English system, is air at 60° F. and 30 inches pressure, or, according to the French system, 0° C. and 760 millimetres.

The **standard for gases in physical and chemical investigations** is hydrogen at 0° C. and 760 millimetres pressure.

English System.

1 cubic inch of water weighs 252.45 grains at 62° F. and 30 inches pressure.

1 cubic foot of water weighs 62.5 pounds at 62° F. and 30 inches pressure.

100 cubic inches of air weigh 30.935 grains at 60° F. and 30 inches pressure.

100 cubic inches of hydrogen weigh 2.14 grains at 60° F. and 30 inches pressure.

Metric System.

1 cubic centimetre of water weighs 1 gramme at 4° C. and 760 millimetres pressure.

1 litre of water weighs 1 kilogramme at 4° C. and 760 millimetres pressure.

1 litre of air weighs 1.2936 gramme at 0° C. and 760 millimetres pressure.

1 litre of hydrogen weighs 0.0896 gramme at 0° C. and 760 millimetres pressure.

Air is 14.44 times heavier than hydrogen.

Water at 4° C. is 772 times heavier than air at 0° C.

" " 4° C. is 784 " " " " 4° C.

Specific Gravity of Solids.

(*a*) **Of solids heavier than water.**

Theorem of Archimedes: When a solid is immersed in a fluid, it displaces a volume of the fluid equal to its own volume, and weighs as much less as the weight of the fluid displaced.

1. **To determine the specific gravity of a solid heavier than water,** find its weight in air and then in water (under the standard conditions), and divide its weight in air by its loss of weight in water; the quotient will be its specific gravity. The specific gravity of a solid may also be determined by means of Nicholson's hydrometer.

Example: To determine the specific gravity of tin:—

Weight of mass of tin in air,	1078 grains,	
Weight of same in water,	934 "	
Loss in weight,	144 "	equals the

weight of the volume of water displaced, hence—

$$1078 \div 144 = 7.48 = \text{specific gravity of tin.}$$

(*b*) **To determine the specific gravity of solids lighter than water.**

Theorem: If a solid specifically **lighter** than water be placed in that fluid it sinks in the fluid until it displaces a volume of the fluid equal to its own weight, and then remains at rest, or floats. To **submerge** such a body requires a force equal to the difference between its own weight and the weight of an equal volume of water.

Hence, weigh the solid in air, then attach it to a solid, of known weight in water, sufficiently heavy to sink it, and then weigh in water. Divide the weight of the solid in air by its weight in air added to the loss of weight it occasioned in the solid of known weight in water, and the quotient will be the specific gravity.

Example: A piece of cork weighing 10 grains in the air occasions a loss of weight of 30 grains in the solid to which it is attached.

Hence:—

$$10 \div 10 + 30. (40).$$
$$10 \div 40 = 0.25, \text{ specific gravity of cork.}$$

(*c*) **To determine the specific gravity of solids soluble in water.**

To find the specific gravity of a solid **soluble** in water a liquid is selected in which the substance is insoluble.

If the specific gravity of sugar is to be determined, the oil of turpentine is selected, as sugar is insoluble in this liquid.

Example:

Weight of a quantity of sugar in air,	100.00	grains.
Weight of same in turpentine,	45.62	"
Loss in weight,	54.38	"

$$100 \div 54\ 38 = 1.83.$$

The specific gravity of oil of turpentine is 0.87.

Then specific gravity water 1 : 0.87 :: 1.83 : 1.6 = specific gravity of sugar compared with water.

(*d*) **To determine the specific gravity of solids in pulverized condition.**

To determine the specific gravity of a solid in a comminuted state, the specific-gravity bottle (picnometer) is used.

In all such experiments it is necessary to pay attention to the temperature and purity of the water, and to remove with great care all adhering air bubbles, otherwise an erroneous result will be obtained.

Specific Gravity of Liquids.

The specific gravity of a liquid is its relative weight compared with the weight of an equal volume of water, under the standard conditions.

(*a*) The specific gravity of a **liquid** may be determined by the **specific-gravity bottle** (picnometer).

Employ a bottle or flask of known weight and the weight of which when filled to a certain mark with pure water has been determined. Place in the dry bottle an equal volume of the liquid under examination and determine its weight. Divide the weight of the liquid by the weight of an equal volume of water, and the quotient represents the specific gravity of the liquid.

A flask or bottle (picnometer) holding 1000 grains of water is generally used for this purpose. The bottle may have a thermometer attached.

Example: Suppose the 1000-grain bottle filled with sulphuric acid contained 1845 grains of that liquid, then

$$1845 \div 1000 = 1.845 \text{ specific gravity of the acid.}$$

(*b*) The specific gravity of a **liquid** may be determined by means of a **hydrometer.**

The specific gravity of liquids may be determined by means of an instrument termed a hydrometer, which is a glass instrument terminating in a bulb containing shot or mercury. The tube of the instrument contains a scale with numbers which express the specific gravity, so that no computation is necessary. 1000 is taken as the fixed point (specific gravity of water).

The hydrometer will sink in a liquid until it displaces a volume of the liquid equal to its own weight, or until it reaches a depth where the buoyant force of the liquid is equal to the weight of the hydrometer.

The specific gravity of liquids both **heavier** and **lighter** than water may be determined in this manner.

The same instrument may have two scales, as the **Universal hydrometer,** one for liquids heavier, the other for liquids lighter, than water.

For accurate determinations the scale is extended over a long spindle, or the scale may be distributed through the spindles of a series of hydrometers.

A **urinometer** is a hydrometer with a limited scale, used for determining the specific gravity of urine. The numbers on the scale usually range between 1000 and 1060. A urinometer when placed in distilled water, under standard conditions, should sink exactly to the 1000 point.

Specific Gravity of Gases.

The specific gravity of gases is compared with air or with hydrogen at 60° F. and 30 inches pressure, or 0° C. and 760 millimetres pressure.

The specific gravity of a substance in the gaseous state is employed to determine the molecular weight of the substance.

Method: Fill a large glass flask or globe with the pure and dry gas, weigh it, and at the same time observe the temperature of the surrounding air and the barometric pressure. Exhaust the globe by means of an air pump and again weigh. Finally, fill it with dry air and weigh it, the temperature and pressure being known. On the supposition that the temperature and pressure are the same in both cases, the specific gravity is at once obtained by dividing the weight of the gas by the weight of the air; if otherwise, correct for temperature and pressure.

Victor Meyer has devised a method and apparatus for the determination of the vapor density of substances.

The specific gravity (compared with air) of the lightest substance known (a gas), hydrogen, is 0.0693.

The specific gravity (compared with air) of the heaviest gas known, aluminium iodide, is 28.15.

Extremes of Specific Gravity.

Solids,	Iridium,	21.8
	Cork,	0.24
Liquids,	Mercury,	13.596
	Cymogen,	0.59
Gases, (Compared with air)	Aluminium Iodide,	28.15
	Hydrogen,	0.0693

2. ATTRACTION OF AGGREGATION (COHESION).

This is a force existing between **similar** molecules of matter and manifesting itself through inappreciable distances. Hardness and softness depend upon this fact.

In no two solids is the attraction of aggregation or cohesion the same.

Properties of solids depending upon attraction of aggregation:

(*a*) Tenacity.
(*b*) Ductility.
(*c*) Hardness.
(*d*) Flexibility.
(*e*) Malleability.

Table of Tenacities,

Showing the weight necessary to rupture wires of different metals $\frac{1}{16}$ of an inch in diameter and an inch in length. (The force of attraction of aggregation existing between the molecules of a metal.)

Iron	ruptures at	549	pounds.
Copper	"	302	"
Silver	"	187	"
Tin	"	36	"
Lead	"	27	"

(*a*) **Solids** are either
1. Crystallizable, or
2. Uncrystallizable.

Crystallization is an example of the attraction of aggregation. **All crystalline forms may be arranged in six systems:**

1. Monometric (cubic).
2. Dimetric.
3. Rhombohedral.
4. Trimetric (rhombic).
5. Monoclinic.
6. Triclinic.

Substances having the same crystalline form are **isomorphous.** A substance capable of crystallizing in two distinct forms, belonging to different systems, is **dimorphous.**

Allotropism is the property possessed by some substances of existing in two or more forms having the same chemical composition, but different physical and, in some cases, physiological properties.

Examples: Sulphur, phosphorus, carbon (diamond and charcoal). Such modifications are said to be **allotropic.**

(*b*) **Liquids**: The attraction of aggregation exists in liquids, but varies considerably, as illustrated in the size of the drops of different liquids.

(*c*) **Gases**: The attraction of aggregation is absent. The molecules repel one another.

3. HETEROGENEOUS ATTRACTION (ADHESION).

A force existing between certain **dissimilar** molecules of matter and manifesting itself only through inappreciable distances.

(*a*) **Solids**: Examples—Glue, cement, etc.

(*b*)—**Liquids**: Examples—Alcohol added to water soon diffuses through the entire quantity of water; is said to be soluble in water. Alcohol is soluble in water in unlimited quantity.

Ether is soluble in ten times its volume of water; if more ether be added it will not dissolve, but will collect on the surface of the water. In this case the heterogeneous attraction is limited.

Oil and water have little or no heterogeneous attraction for each other.

(*c*) **Gases**: All gases have an attraction for one another.

Law of diffusion of gases: The heterogeneous attraction is inversely as the square roots of the densities of the gases.

Example: Hydrogen is 16 times lighter than oxygen, and will diffuse four times more rapidly than oxygen.

This is a wise provision of nature, as otherwise carbon dioxide, a poisonous gas, would collect nearest the earth, the oxygen coming next and the nitrogen last; but they become mixed in nature according to this law.

(*d*) **Solids and liquids:** Water adheres to a glass rod, owing to the water having a heterogeneous attraction for the glass. Mercury will not adhere to the glass because it possesses no heterogeneous attraction for the glass.

A liquid will dissolve a solid only when the adhesion between the liquid and the solid is greater than the cohesion in the solid.

When sugar and water are mixed the heterogeneous attraction existing between the molecules of sugar and the molecules of water is greater than the attraction of aggregation possessed by the sugar itself and, as a result, the sugar dissolves, forming a solution.

Water has the greatest range of solvency of any liquid known. When reference is made to the solubility of a substance, water is always understood to be the solvent, unless another liquid is specified.

Some substances are soluble, others partly soluble, and some insoluble.

The dissolving liquid is called a **solvent,** and the resulting liquid is called a **solution.** Thus, one part of the following compounds requires about the following quantities of water for solution:

Barium sulphate about	200,000 parts.
Strontium sulphate about	10,000 "
Calcium sulphate "	500 "
Magnesium sulphate "	2 "

When 1 part of a substance is soluble in 100 parts of water it is termed soluble.

The dissolving of a substance is facilitated by its being in a finely comminuted state, as thus more surface is brought in contact with the dissolving agent.

Temperature affects the solubility of a substance. With few exceptions, hot liquids dissolve substances more rapidly and in greater quantity than cold liquids.

Lime is more soluble in cold water than in hot water.

A **saturated solution** is one that holds in solution all of a substance that it possibly can at a given temperature.

When a liquid containing a solid in solution is brought in contact with another liquid possessing a greater heterogeneous attraction for the liquid than for the solid, the solid will separate as a precipitate.

Example: When an alcoholic solution of camphor is brought in contact with water, the camphor is precipitated.

Certain organic coloring matters may be removed from liquids by means of animal charcoal. Alkaloids may also be separated from liquids by animal charcoal.

Osmosis: When liquids pass through a porous diaphragm and mix with each other, the diffusion is called **Osmosis.** To distinguish the two opposite currents, the flow of the liquid toward that which increases in volume is called **Endosmosis,** and the opposite current is called **Exosmosis.**

The process of separating mixed liquids by osmosis is called dialysis.

Dialysis: The gradual passage through a membrane of a dissolved substance from its original solution into pure water is called **dialysis.** Parchment paper is usually the membrane employed, and may be prepared by dipping unsized paper a moment in a cold mixture of one volume of water and two volumes of sulphuric acid, then washing it thoroughly with water and afterward with water containing a little ammonia, and drying.

Those substances which pass through membranes are called **crystalloids**; those which do not pass through are called **colloids.**

(*e*) **Solids and gases:** Certain solids possess so strong an attraction for gases that they not only draw the gases into the small cavities within them, but to a considerable extent condense them there.

Spongy platinum absorbs (occludes) oxygen. Palladium occludes hydrogen. Magnesium oxide and iron filings do not sink when thrown on water, owing to the heterogeneous attraction existing between those substances and air.

Charcoal readily absorbs gases. It is especially useful in removing noxious gases in hospitals or in the sick-room, and in absorbing noxious odors from putrid animal and vegetable matter. It does not check decay, but rather hastens it.

Table of the Volume of Gases Absorbed by One Cubic Inch of Charcoal.

Ammoniacal gas,	90	cubic inches.
Hydrochloric acid gas,	85	"
Hydrogen sulphide,	55	"
Carbon dioxide,	35	"
Oxygen,	9	"
Hydrogen,	1.7	"

(*f*) **Liquids and gases** may combine, due to:

1. **Chemical combination** of a liquid and a gas,—in such cases the amount of each entering into combination is definite.

2. **Physical combination** of a liquid and a gas, due to:

a. Nature of liquid and gas.
b. Temperature of liquid and gas.
c. Pressure of gas.

The amount of gas a liquid will absorb is increased by pressure. "Soda water" or carbonated water is simply water saturated with carbon dioxide under great pressure; when the pressure is removed, a large part of the gas escapes, producing effervescence.

Coefficient of Absorption of Gases by (One Vol.) Water.

Gas.	O.	H.	N.	CO_2.	CO.	H_2S.	SO_2.	NH_3	HCl.	Air.
At 0° C.	0.0411	0.0193	0.0203	1.796	0.0328	4.370	68.861	1049.6	503.0	0.0247
10° C.	0.0325	0.0193	0.0160	1.231	0.0258	3.585	51.383	794.3	469.0	0.0195
15° C.	0.0299	0.0193	0.0147	1.002	0.0240	3.232	43.564	711.8	454.0	0.0179

When **two** or **more** neutral gases are brought in contact with a neutral liquid, a **portion** of each gas is absorbed; but not to the same extent as either gas would be, if alone,—since in a **mixture** of gases there is only a **partial pressure** of each gas.

Atmospheric Air in Water.

Composition of air; say 0.21 % **O** + 0.79 % **N**. Hence at 0°C

O = 0.21 × 0.0411 = 0.008631 vol. **O** absorbed.
N = 0.79 × 0.0203 = 0.016037 " **N** "
0.024668 " **O** + **N** absorbed.

0.024668 : 0.008631 :: 1 : 0.3497 proportion of **O** absorbed.
0.024668 : 0.016037 :: 1 : 0.6503 " " **N** "

Hence the **absorbed air** consists of 0.3497 of **O** + 0.6503 of **N**
whereas **ordinary air** " " 0.21 " " + 0.79 " "

4. CHEMICAL ATTRACTION OR FORCE (CHEMISM).

An attraction existing between the atoms of certain dissimilar substances acting through inappreciable distances to form new compounds.

$$H_2O + SO_3 = H_2SO_4$$
$$H_2SO_4 + K_2O = K_2SO_4 + H_2O$$
$$HCl + NH_3 = NH_4Cl.$$

HEAT.

Heat is a mode of motion (molecular motion).

1. **Corpuscular theory of heat**: That heated substances send out small particles of matter in straight lines, which, by their impingement, produce the sensation of heat.

2. **Undulatory theory**: That heat is given off in wave-like undulations from bodies.

Sources of heat:

1. **The sun** (solar heat).
2. **The earth** (terrestrial heat).
3. **Mechanical action.**
4. **Chemical action.**

Terrestrial heat: Observations made during two centuries show that solar heat affects the temperature of the earth to a depth about 88.6 feet below the surface, at which depth the temperature remains constant at 53.5° F. In descending toward the centre of the earth below the depth of 88.6 feet

the temperature increases about 1° F. for every 54 feet of depth. The rate of increase of temperature varies in different parts of the world.

Mechanical action: Mechanical motion checked becomes heat.

Examples: Hammer a piece of iron and it soon becomes hot. Fire may be obtained by rubbing together two pieces of dry wood (friction).

To heat 1 pound of water through a range of 1° F. requires the expenditure of a mechanical force equivalent to that produced by the falling of a body weighing 772 pounds a distance of 1 foot; or to heat 1 gramme of water 1° C. is equivalent to the mechanical force produced by a body weighing 423.65 grammes falling a distance of 1 metre (about 40 inches).

The heat unit generally employed is the amount of heat required to raise the temperature of 1 kilogramme of water from 0° C. to 1° C. This unit is called a **calorie.**

Chemical action: Chemical action is always accompanied by a change of temperature. The change of temperature may or may not be evident. Chemical combination may occur with lowering of temperature.

Combustion: Combustion is chemical combination attended with the evolution of heat and light. (Chemical combination is not necessarily combustion.)

Elementary substances may be divided into—

1. **Combustible:** (Types—carbon, sulphur, hydrogen.)

2. **Supporters of combustion:** (Type—oxygen.)

3. **Indifferent;** Substances which are neither combustible nor supporters of combustion. Most of the elements belong to this class.

The quantity of heat developed in the combustion of different substances varies.

1 gramme of hydrogen when burned with an adequate quantity of oxygen develops sufficient heat to raise the temperature of 34,462 grammes of water from 0° C. to 1 C. (*i. e.*, through a range of 1° C.).

Table Showing the Amount of Water the Temperature of which can be Raised from 0° C. to 1° C. by the Combustion with Oxygen of 1 Gramme of Different Substances.

Hydrogen,	34,462	grammes water.
Carbon,	8,080	" "
Phosphorus,	5,747	" "
Sulphur,	2,221	" "
Marsh gas,	13,063	" "
Alcohol,	6,909	" "
Ether,	9,027	" "

Before combustion will take place, a certain amount of heat must be applied.

Different substances require different temperatures to bring about combustion.

In combustion, gaseous matter is not luminous until a temperature of about 2000° F. is reached.

Solids are red-hot at a temperature of about 900° F.

EFFECTS OF HEAT.

Temperature is the manifestation of heat: A very large amount of heat may be present and the substance have a very low temperature, and **vice versa.**

The tendency of heat is to augment the volume of matter by increasing the intermolecular spaces.

(*a*) **Solids:** As a rule, all solids expand on the application of heat. No two solids expand equally.

Table Showing the Expansion in Volume of Solids When Heated from 32° F. to 212° F.

Glass,	$\frac{1}{1248}$
Platinum,	$\frac{1}{1131}$
Iron,	$\frac{1}{846}$
Gold,	$\frac{1}{682}$
Silver,	$\frac{1}{524}$
Lead,	$\frac{1}{351}$
Mercury,	$\frac{1}{55}$

(*b*) **Liquids**; All liquids expand on the application of heat, but no two expand equally.

Heated from 32° F. to 212° F.—

Mercury expands $\frac{1}{55}$ of its volume.
Water " $\frac{1}{23}$ " "
Alcohol " $\frac{1}{8}$ " "

Water is at its maximum density at 4° C. (39.2° F.)

Water at 0° C., when heated to 1° C., contracts and continues to contract until 4° C. is reached, when its volume is least. Heated beyond 4° C., it expands.

(*c*) **Gases**; All gases expand equally for equal increments of heat.

The actual amount of expansion is equal to $\frac{1}{273}$ or $\frac{11}{3000}$ of the volume of the gas for each degree Centigrade, and about $\frac{1}{490}$ of the volume for each degree Fahrenheit above 32° F.

273 volumes of a gas at 0° C. become 274 at 1° C.
273 " " " 275 at 2° C.
273 " " " 289 at 16° C.

Or—

3000 volumes of a gas at 0° C. become 3011 at 1° C.
3000 " " " 3022 at 2° C.
3000 " " " 3176 at 16° C.

Thermometers.

Measurers of temperature.

Heat is the term applied to the agent itself.

Temperature is the manifestation of heat.

In determining temperature, advantage is taken of the property of expansion of **solids, liquids** and **gases**.

Mercury is the liquid usually employed in thermometers, because of its having a great range of liquidity and of its regularity of expansion within certain limits. It is also very sensitive to heat. At high temperatures it does not expand equally, but its unequal expansion is nearly compensated by the expansion of the glass thermometer tube.

The first mercurial thermometer was constructed by Fahrenheit, in 1714. Réaumur followed in 1730 and Celsius in 1742. The one constructed by the latter is also called the Centigrade (*one hundred steps*) thermometer, and is employed almost universally in scientific investigations.

Fahrenheit made a mixture of two parts of ice and one of salt, and believed the temperature thus obtained to be the lowest attainable. He introduced a glass tube containing mercury into this mixture, and designated the height at which the mercury stood in the tube as the zero point. From this point to the freezing point of water the mercury expanded 32 parts in 10,000 parts. On this account he designated the freezing point of water by the number 32.

The tube containing the mercury was next introduced into boiling water, and it was found that, from the assumed zero point to the boiling point of water, the mercury in the tube had expanded 212 parts in 10,000, and on this account the boiling point of water was designated by the number 212.

There are three systems of thermometers;

	Zero Point.	Freezing Point.	Boiling Point.	Relation to each other.
1. Fahrenheit, ...	0°	32°	212°	9
2. Réaumur, ...		0°	80°	4
3. Centigrade (Celsius), . . .		0°	100°	5

To convert degrees of one system into another.

Fahrenheit into Centigrade: Deduct 32 from the temperature F., multiply by 5 and divide by 9.

$$-32 \times 5 \div 9.$$

Example:

$$\text{F. } 212^\circ - 32^\circ = 180^\circ \times 5 = 900^\circ \div 9 = 100^\circ \text{ C.}$$

Convert minus 40° F. into C.

$$-40^\circ + -32^\circ = -72^\circ \times 5 = -360^\circ \div 9 = -40^\circ \text{ C.}$$

Fahrenheit into Réaumur: Deduct 32 from the temperature F., multiply by 4 and divide by 9.

$$-32 \times 4 \div 9.$$

Centigrade into Fahrenheit: Multiply the temperature C. by 9, divide by 5 and add 32.

$$\times 9 \div 5 + 32.$$

The stem of a mercurial thermometer should be free from air. Its freedom from air may be determined by inverting the thermometer, and observing whether the mercury runs down to the end of the tube, with the production of a clicking sound. If the mercury will not run down to the end of the tube, it may be taken as evidence of the presence of air.

The smaller the calibre of the tube containing the mercury the more sensitive the thermometer.

Mercury freezes at —40° C. or —40° F. The Fahrenheit and Centigrade scales do not correspond at any other point.

Alcohol thermometers (spirit thermometers) are mainly used for determining very low temperatures.

Air thermometers are the most sensitive of all thermometers. These instruments are sensitive to the $\frac{1}{6000}$ of a degree F.

Solids, as a bar of metal (platinum, etc.), are employed in the construction of instruments for determining very high temperatures. Such instruments are called **pyrometers.**

Differential thermometers are used to determine differences of temperature between two portions of air.

Registering thermometers are for the purpose of registering maximum and minimum temperatures.

The clinical thermometer is a form of registering thermometer.

Equalization of Temperature.

May occur in three ways:

1. Conduction.
2. Convection.
3. Radiation.

1. Conduction: The flow of heat through an unequally heated body from places of higher to places of lower temperature.

Different bodies possess very different conducting powers with respect to heat.

(*a*) **Solids:** Copper is a good conductor. Glass is a poor conductor.

Table of Conduction of Heat by Solids.

Silver, ...	1000	Tin, ...	145
Copper, ...	736	Iron, ...	119
Gold, ...	532	Lead, ...	84
Zinc, ...	190	Bismuth, . . .	18

(*b*) **Liquids,** as a rule, are poor conductors. The water contained in the upper part of a glass tube may be brought to the boiling point while the liquid just below is of ordinary temperature.

(*c*) **Gases** are poor conductors.

2. **Convection:** The transference of heat from one place to another by the bodily moving of heated substances. The term convection is rarely applied to solids. Solids require some external force to effect the conveyance; liquids and gases do not.

Water and gases are heated by convection. In heating water, the lower portion in the vessel becomes heated, expands, and thereby becomes less dense than the liquid above, consequently it rises, forming an upward current, while the cooler liquid above descends to take its place.

3. **Radiation:** The emission of heat, from a heated body, in straight lines or rays which pass through air without interruption, and become absorbed by neighboring objects which happen to be presented to their impact.

The power of radiation varies with different bodies. A rough surface is a better radiator than a polished surface. Color often affects the power of radiation.

Transmission of Heat.

1. **Solids:** Solids vary in their power of transmitting heat. Rock-salt and air are the only substances known that are equally transparent or diathermous to all kinds of heat rays.

2. **Liquids:** Water absorbs a great amount of heat, and it is owing to this fact that a moist atmosphere at a given temperature seems colder than dry air at the same temperature.

0.4 per cent of water (moisture) in the atmosphere will absorb as much heat as is absorbed by the air through which the heat passes.

3. **Gases:** Gases vary in their power of transmitting heat. Hydrogen absorbs the greatest amount of heat of any gas known.

One-fifth of the solar heat is absorbed in passing through a layer of air 6000 feet in thickness.

The dew point: When air contains such an amount of vapor of water that its temperature cannot be lowered without some of the vapor being precipitated in the liquid form, the air is said to be saturated, and the **temperature** is called the **dew point.**

The quantity of water which the air is capable of absorbing depends upon the temperature of the air Air at 32° F. is capable of holding about $\frac{1}{160}$ of its weight of water, and its capacity is doubled for about every 27° F.

To determine the dew point, cover the mercury bulb of a thermometer with a piece of wet muslin or of cotton, and swing the instrument several minutes to and fro in the air. The temperature indicated by the thermometer when the mercury ceases to sink is the dew point. The dew point is usually 10° C. to 15° C. below the actual temperature of the air.

To determine the degree of saturation of the air by aqueous vapor: Divide the tension of the aqueous vapor at the dew point by the tension of the aqueous vapor at the observed temperature of the air.

Thus, if the temperature of air = 20° C.
and dew point, = 15° C.
Tension of vapor at 20° C. = 17.391 millimetres.
" " " 15° C. = 12.699 "

Hence, 12.699 ÷ 17.391 = 0.73 degree of saturation or **humidity.**

CAPACITY FOR HEAT.

Capacity for heat or specific heat: To produce equal degrees of temperature in equal weights of different substances, different amounts of heat are required. For example, it requires more heat to raise the temperature of one pound of water from 0° C. to 1° C. than to produce the same change of temperature in the same weight of mercury.

The relative amount of heat required to raise equal weights of substances through equal degrees of temperature is called **specific heat.**

Methods of determining specific heat.

1. Observing the quantity of ice melted by a given weight of the substance heated to a certain temperature.

2. Noting the time which the heated body requires to cool down through a certain number of degrees.

3. Subjecting different substances to the same amount of heat.

4. Mixing liquids of different temperatures and observing the temperature of the mixture.

Examples:

(*a*) 1 pound of water at 100° C.
1 " " " 40° C.
2)140
Temperature of the mixture, 70° C.

(*b*) 1 pound of water at 100° C.
1 " olive oil at 40° C.

The temperature of this mixture is not the mean of the two temperatures (70° C.), but 80° C., showing that water has about twice the capacity for heat that oil has.

(*c*) 1 pound of water at 100° C.
1 " mercury at 40° C.

The temperature of this mixture is 98° C.

Freezing mixtures:

2 parts snow and 1 part sodium chloride reduce temp. to —4° F.
2 " " " 3 parts calcium chloride " " to —50° F.

Specific heat of solids and liquids: Water has the greatest capacity for heat of all solids and liquids.

Gases differ in their capacity for heat.

Hydrogen has the greatest capacity for heat of any known substance.

Table Showing the Specific Heat of Certain Solids and Liquids.

(Water, taken as standard, 1000°.)

Solids.		Liquids.	
Charcoal,	241°	Alcohol,	505°
Iron,	113°	Chloroform,	230°
Zinc,	95°	Bromine,	106°
Mercury,	33°		

Hydrogen has the highest specific heat, 5880°.

Uranium has the lowest specific heat, 27°.

241° of heat applied to a certain weight of charcoal will indicate the same increase of temperature as 1000° applied to the same weight of water.

LATENT HEAT.

Latent heat is heat not manifesting itself as temperature. Bodies absorb a certain quantity of heat which is not indicated by the thermometer.

Example ;

$$\left.\begin{array}{llll}\text{1 pound} & \text{of water at} & & 0^\circ\text{ C.}\\ \text{1 "} & \text{"} & \text{"} & 79^\circ\text{ C.}\end{array}\right\} = \text{2 pounds of water at 39.5 C.}$$

$$\left.\begin{array}{llll}\text{1 "} & \text{of ice} & \text{"} & 0^\circ\text{ C.}\\ \text{1 "} & \text{of water} & \text{"} & 79^\circ\text{ C.}\end{array}\right\} = \text{2 " " " " } 0^\circ\text{ C.}$$

In the latter example, a change of state has occurred. A certain solid, ice, is converted into a liquid. It requires 79° C. to convert ice at 0° C. into water at 0° C., *i. e.*, as much heat has been rendered latent as would heat an equal weight of water from 0° to 79° C.

Whenever a change in state of aggregation occurs, heat is either rendered latent or latent heat is made manifest.

1. **Solid to liquid state :** A solid can never become liquid until a certain amount of heat is applied, which is rendered latent.

2. **Liquid to gaseous state :** Heat is rendered latent, as in the case of solids.

Example : Water heated to boiling cannot be heated above 100° C. at ordinary atmospheric pressure, (at the level of the sea) no matter how much heat be applied.

A liquid boils when a vapor is produced of sufficient tension to overcome the attraction of aggregation and pressure upon the liquid.

The density of a liquid does not control its boiling point. As the attraction of aggregation differs in liquids, so does the boiling point.

Pressure influences the boiling point. The boiling point diminishes as the pressure diminishes, and increases as the pressure increases.

Water boils at elevated places at a lower temperature than at the level of the sea. In some elevated places water boils at a temperature lower than that required to coagulate the albumin of an egg. (For example, at Quito, in Ecuador.)

Certain salts in solution in water increase the boiling point because of the increase in the attraction of aggregation.

3. **Gaseous to liquid state:** Before gases become liquid, latent heat is developed which manifests itself as temperature.

Steam at 100° C., before it becomes **water** at 100° C., must give up heat sufficient to heat 536.5 times its weight of water from 0°C. to 1° C. This is termed the **latent heat of steam.**

4. **Liquid to solid state:** When a liquid changes to the solid state a certain amount of heat is made manifest.

Example: The slaking of lime.

$$CaO + H_2O = Ca(OH)_2.$$

CHEMISTRY.

Chemistry is the science which treats of the properties and laws relating to the ultimate molecules and atoms of matter.

All **matter** is made up of **molecules,** and molecules are made up of **atoms.**

All matter as found in nature is either elementary or compound.

Elementary matter or an **element** is matter in which the molecules are composed of atoms **similar** in kind, *i. e.*, matter which cannot be resolved into anything simpler.

Iron, gold and hydrogen are examples of elementary matter. These substances cannot be resolved into anything simpler.

Compound matter is matter in which the molecules are composed of atoms **dissimilar** in kind, *i. e.*, matter which may be resolved into simpler matter.

Water and common salt are examples of compound matter. By appropriate means water may be resolved into simpler matter—two gases, hydrogen and oxygen, but these gases being elementary forms of matter cannot be resolved into anything simpler.

The **great mass of matter** is in the **compound state.** There are from 65 to 70 **elementary substances** known at present. Some of these elementary substances are rare, while others are widely distributed.

Oxygen is the most widely distributed element in nature, occurring in most of the mineral and vegetable structures. Lithium is one of the rarer elements.

Most compound substances are composed of but a few of these elements.

Elementary forms of matter or **elements** in chemistry are represented by symbols, formed generally of the initial letter of the Latin name of the element, as O = oxygen, H = hydrogen, Hg = (hydrargyrum) mercury, C = carbon, Na (natrium) = sodium.

The **symbol represents** not only the **element** itself, but also a **definite** quantity of it by weight, called the **atomic weight.** It also represents the **valence** of the **element.**

Each symbol represents **one atom** of the element for which it stands, and consequently expresses a definite weight and volume of the element.

The weight of an atom of hydrogen is less than the weight of an atom of any other element. For convenience, the value of the symbol of hydrogen (1) is considered as unity, and the values of all other symbols as greater than unity. (Na = 23. Cl = 35.5. O = 16.)

Chemical combination: In order to indicate combination between two or more elements their symbols are placed side by side, thus, HCl, hydrochloric acid; $NaCl$, sodium chloride. When a molecule of a compound contains more than one atom of each or any of its constituents, the number of atoms is indicated by a small figure placed below the line and directly to the right of the symbol.

Thus, the formula for water, H_2O, represents two **atoms** of hydrogen united with one **atom** of oxygen, and Na_2SO_4 means that two **atoms** of sodium, one **atom** of sulphur and four **atoms** of oxygen are bound together in sodium sulphate.

The formula, taken as a whole, is generally assumed to represent a molecule of the compound. The relative weight of the molecule is easily found by adding together the atomic weights represented by the several symbols of which it is made up. This weight is called the molecular weight. In order to express two or more molecules a figure is placed at the beginning of the formula, and must be understood to multiply every symbol that follows it. For example, $3H_2O$ represents three molecules of water, each consisting of two atoms of hydrogen with one atom of oxygen; in all six atoms of hydrogen and three atoms of oxygen. Occasionally brackets have to be introduced when some group of symbols occurs more than once. Ferric sulphate, for example, has the formula $Fe_2(SO_4)_3$.

The **elements** are **divided** into **two classes—metals** and **non-metals.**

The **metals** are **electro-positive.**

The **non-metals** are **electro-negative.**

For example, when a current of electricity is passed through water, decomposition of the water occurs, hydrogen is evolved at the negative pole, and oxygen at the positive pole; therefore hydrogen is termed positive and oxygen negative.

The **elements differ** in their **electrical intensity. Cæsium** is the **strongest** of the **electro-positive** elements. **Oxygen** is the **strongest** of the **electro-negative** elements.

Examples of Electro-Positive Elements Arranged in the Order of their Electrical Intensity.

Cæsium (strongest electro-positive).
Rubidium.
Potassium.
Sodium.
Lithium.

The **elements** are also **divided** into groups according to their **valence** or **saturating power** compared with hydrogen as unity, *i. e.*, **Monads, Diads, Triads, Tetrads, Pentads, Hexads,** and **Heptads.**

Elements having an even valence are termed **artiads,** and those having an odd valence are termed **perissads.**

The elements may be arranged in groups based on the increase of their atomic weights according to the Periodic Law of Mendelejeff.

Chemical compounds are always **definite** in **composition.**

Example: The molecule of water (H_2O) is composed of two atoms of hydrogen and one atom of oxygen. The composition of water never varies from this. The formula H_2O **does not mean two parts by weight of hydrogen and one part by weight of oxygen,** but represents two parts by weight (twice the atomic weight) of hydrogen in combination with sixteen parts by weight (once the atomic weight) of oxygen. The formula Na_2SO_4, sodium sulphate, represents twice the atomic weight or forty-six parts by weight of sodium in combination with once the atomic weight, or thirty-two parts by weight of sulphur, and four times the atomic weight or sixty-four parts by weight of oxygen.

Chemical combination takes place between elements because of the difference in their electrical conditions. An electro-positive element may combine with an electro-negative element to form a compound, as $\overset{+}{Ca}$ with $\overline{O} = Ca\,O$.

A strong electro-positive element may displace a weaker electro-positive element, as—

$$K_2 + H_2O = K_2O + H_2,$$

and a strong electro-negative element may displace a weaker electro-negative element.

Elements in the same electrical condition may enter into combination with each other. In such a case one of the elements must be stronger electrically than the other, and thus throw the weaker into the opposite electrical condition.

Example: Negative sulphur may unite with negative oxygen to form the compound sulphurous anhydride.

$$\overline{S} + \overline{O}_2 = SO_2.$$

In this example the sulphur is thrown into the electro-positive condition.

In chemical combination it does not necessarily follow that the resulting compound is neutral. The negative or the positive property may predominate, or the compound may be neutral.

K_2O, potassium oxide, a compound having positive properties.

SO_3, sulphuric anhydride, a compound having negative properties.

MnO_2, manganese dioxide, a neutral compound.

CLASSIFICATION OF INORGANIC COMPOUNDS.

Inorganic compounds, with very few exceptions, may be considered as belonging to one of **three classes :**

I. **Oxides,** example, K_2O.
II. **Acids,** " HCl.
III. **Salts,** " $NaCl$, Na_2SO_4.

I. OXIDES.

An **oxide** is a binary compound (*i. e.*, made up of two elements), one of which is oxygen.

There may be oxides of all the elements except fluorine.

There are **three groups of oxides :**

(*a*) **Basic** oxides.
(*b*) **Neutral** oxides.
(*c*) **Oxyacid** radicals.

(*a*) **Basic oxides** are oxides of the metals in which the intensity of the positive element predominates. (All oxides of the metals are not basic oxides.) Basic oxides turn red litmus paper blue.

(*b*) **Neutral oxides** are oxides in which the elements just neutralize each other. There are neutral oxides of the non-metallic elements and of the metals.

(*c*) **Oxyacid radicals** are oxides of the non-metallic elements (except H and Fl) and higher oxides of weaker electro-positive metals. Hydrated oxyacid radicals change blue litmus paper red.

A **radical** is a chemical combination of two or more elements capable of playing the part of an elementary form of matter.

(*a*) **Basic oxides** follow **one or other** of five forms :

1. **Two** atoms of the metal with **one** of oxygen, called **suboxide,** as, K_2O, Na_2O, Ag_2O, etc.

2. **One** atom of the metal with **one** of oxygen, called **protoxide,** as, CaO, BaO, CuO, etc.

3. **Two** atoms of the metal with **three** of oxygen, called **sesquioxide,** as, Fe_2O_3, Al_2O_3, Cr_2O_3, etc.

4. **One** atom of the metal with **two** atoms of oxygen, called **binoxide,** as, PbO_2, IrO_2, PtO_2, etc. They are feebly basic and sometimes act as acid radicals.

5. **One** atom of the metal with **three** atoms of oxygen, called **trioxide,** as, UrO_3.

(*b*) **Neutral oxides** may be oxides of the metals or of the non-metals. They do not change litmus.

Examples :

H_2O, CO, MnO_2, PbO_2.

(*c*) **Oxyacid radicals** are mostly oxides of the non-metals. Only a few are oxides of the metals. There may be several oxyacid radicals of the same element. They are usually called **anhydrides.** They combine with the elements of water to form oxyacids.

The name of an oxyacid radical is determined by the positive element, and the members of a group composed of the same elements are distinguished by the difference in the terminations of the name of the individual members of the group.

The name of the most stable compound of the group terminates in **ic.** The compound containing less oxygen in proportion to the positive than the compound terminating in **ic,** terminates in **ous.** The compound under the **ous** compound in the proportion of oxygen, is prefixed by **hypo** and terminates in **ous.** The compound above the **ic** compound in the proportion of oxygen, is prefixed by **hyper** and terminates in **ic.**

Examples.

Anhydrides of Sulphur:

SO,	**Hypo**sulphur**ous** anhydride or oxide. (Has never been isolated.)
SO_2,	Sulphur**ous** " " "
SO_3,	Sulphur**ic** " " "
S_2O_7,	**Hyper**sulphur**ic** " " "

Anhydrides of Chlorine:

Cl_2O,	**Hypo**chlor**ous** anhydride or oxide.
Cl_2O_3,	Chlor**ous** " " "
Cl_2O_5,	Chlor**ic** " " "
Cl_2O_7,	**Hyper**chlor**ic** " " "

Anhydrides of Nitrogen:

N_2O,	**Hypo**nitr**ous** anhydride or oxide.
N_2O_3,	Nitr**ous** " " "
N_2O_5,	Nitr**ic** " " "

Anhydrides of Phosphorus:

P_2O,	**Hypo**phosphor**ous** anhydride or oxide.
P_2O_3,	Phosphor**ous** " " "
P_2O_5,	Phosphor**ic** " " "

Anhydrides of Arsenic:

As_2O_3,	Arsen**ious** anhydride.
As_2O_5,	Arsen**ic** "

Anhydrides of Chromium:

CrO_3,	Chrom**ic** anhydride or oxide.
Cr_2O_7,	**Hyper**chrom**ic** " " "

Anhydrides of Tin:

SnO_2,	Stann**ic** anhydride or oxide.
Sn_5O_{10},	**Meta**-stann**ic** " " "

II. ACIDS.

An **acid** is a chemical compound capable of uniting with and neutralizing a base.

All acids contain hydrogen.

Acids may be divided into **two classes**:

1. **Hydrogen acids.**
2. **Oxyacids.**

1. A **hydrogen acid** is a binary compound containing hydrogen in combination with one of the following electro-negative elements, viz., Cl, I, Br, Fl, S, Se, Te, and As, Sb, P.

They may be named by giving the name of the electro-positive element first, as HCl, hydrochloric acid, or by reversing and giving the name of the electro-negative element first, as HCl, chlorhydric acid. The names of all hydrogen acids terminate in **ic**, but all acids terminating in **ic** are not necessarily hydrogen acids.

Examples.

Monivalent:

HCl,	Hydrochloric acid.
HBr,	Hydrobromic "
HI,	Hydriodic "
HFl,	Hydrofluoric "

Divalent:

H_2S,	Hydrosulphuric acid.
H_2Se,	Hydroselenic "
H_2Te,	Hydrotelluric "

Trivalent:

H_3As,	Hydrogen arsenide.	(Arsenuretted hydrogen.)
H_3Sb,	Hydrogen antimonide.	(Antimonuretted ")
H_3P,	Hydrogen phosphide.	(Phosphoretted ")

2. An **oxyacid** is a hydrate of an oxyacid radical. All oxyacids contain oxygen.

Examples:

Oxyacids of Sulphur, in which one molecule of the oxy-acid radical enters into combination with one molecule of water to form one molecule of acid.

$$\left.\begin{array}{l} SO \\ SO_2 \\ SO_3 \\ S_2O_7 \end{array}\right\} + H_2O = \left\{\begin{array}{ll} H_2SO_2, & \text{Hyposulphurous acid.} \\ H_2SO_3, & \text{Sulphurous } " \\ H_2SO_4, & \text{Sulphuric } " \\ H_2S_2O_8, & \text{Hypersulphuric } " \end{array}\right.$$

Oxyacids of Chlorine, in which one molecule of the oxyacid radical enters into combination with one molecule of water to form two molecules of acid.

$$\left.\begin{array}{l} Cl_2O \\ Cl_2O_3 \\ Cl_2O_5 \\ Cl_2O_7 \end{array}\right\} + H_2O = \left\{\begin{array}{ll} 2HClO, & \text{Hypochlorous acid.} \\ 2HClO_2, & \text{Chlorous} \quad \text{''} \\ 2HClO_3, & \text{Chloric} \quad \text{''} \\ 2HClO_4, & \text{Hyperchloric} \quad \text{''} \end{array}\right.$$

Oxyacids of Nitrogen, in which one molecule of the oxyacid radical enters into combination with one molecule of water to form two molecules of acid.

$$\left.\begin{array}{l} N_2O \\ N_2O_3 \\ N_2O_5 \end{array}\right\} + H_2O = \left\{\begin{array}{ll} 2HNO, & \text{Hyponitrous acid.} \\ 2HNO_2, & \text{Nitrous} \quad \text{''} \\ 2HNO_3, & \text{Nitric} \quad \text{''} \end{array}\right.$$

Oxyacids of Phosphorus, in which one molecule of the oxyacid radical enters into combination with three molecules of water to form two molecules of acid.

$$\left.\begin{array}{l} P_2O \\ P_2O_3 \\ P_2O_5 \end{array}\right\} + 3H_2O = \left\{\begin{array}{ll} 2H_3PO_2, & \text{Hypophosphorous acid.} \\ 2H_3PO_3, & \text{Phosphorous} \quad \text{''} \\ 2H_3PO_4, & \text{Phosphoric} \quad \text{''} \end{array}\right.$$

Oxyacids of Arsenic, in which one molecule of the oxyacid radical enters into combination with three molecules of water to form two molecules of acid.

$$\left.\begin{array}{l} As_2O_3 \\ As_2O_5 \end{array}\right\} + 3H_2O = \left\{\begin{array}{ll} 2H_3AsO_3, & \text{Arsenious acid.} \\ 2H_3AsO_4, & \text{Arsenic acid.} \end{array}\right.$$

III. SALTS.

A **salt** is a compound produced by replacing part or all of the hydrogen of an acid by a metal.

Salts may be arranged in **three groups:**

1. **Simple salts.**
2. **Oxysalts (compound salts).**
3. **Double salts.**

(*a*) A **simple salt** is a binary compound in which the hydrogen of one or more molecules of a hydrogen acid has been replaced by a metal.

8. As_2S_5, K_2S_5,	*i. e.*, two atoms of the positive element in combination with five atoms of the negative element, generally called **penta** compounds. **Example:** Dipotassic pentasulphide.
9. Fe_2Cl_6, Al_2Cl_6,	*i. e.*, two atoms of the positive element in combination with six atoms of the negative element, generally called **sesqui** compounds.
10. $WoCl_6$,	**hexa**-salt, *i. e.*, one atom of the positive element in combination with six atoms of the negative element.

(*b*) An **oxysalt** is a compound resulting from the replacement of part or all of the hydrogen in an oxyacid by a metal.

Example:

1. $H_2SO_4 + KOH = KHSO_4 + H_2O.$
2. $H_2SO_4 + 2KOH = K_2SO_4 + 2H_2O.$

In **naming oxysalts** the name of the positive element precedes the name of the negative. The name of the compound may have the prefix **hyper**, or **hypo**, and may terminate in **ate** or **ite** depending on the particular compound named.

1. Oxyacids terminating in **ic** entering into combination with bases, form salts terminating in **ate.**

Example:

$$\overset{\text{Sulphuric Acid.}}{H_2SO_4} + 2KOH = \overset{\text{Potassium Sulphate.}}{K_2SO_4} + 2H_2O.$$

2. Oxyacids terminating in **ous** entering into combination with bases form salts terminating in **ite.**

Example:

$$\overset{\text{Sulphurous Acid.}}{H_2SO_3} + 2KOH = \overset{\text{Potassium Sulphite.}}{K_2SO_3} + 2H_2O.$$

3. **Oxyacids** having the prefix **hyper** and terminating in **ic,** entering into combination with bases, form salts having the prefix **hyper** and terminating in **ate.**

Example:

Hyperchloric Acid. **Potassium Hyperchlorate.**

$$HClO_4 + KOH = KClO_4 + H_2O.$$

4. Oxyacids having the prefix **hypo** and terminating in **ous**, entering into combination with bases, form salts having the prefix **hypo** and terminating in **ite.**

Example:

Hyposulphurous Acid. **Potassium Hyposulphite.**

$$H_2SO_2 + 2KOH = K_2SO_2 + 2H_2O.$$

Naming of other salts:

$K_2O.CrO_3$, $= K_2CrO_4$, Potassium mono-chromate.
$K_2O(CrO_3)_2$ $= K_2Cr_2O_7$, Potassium di-chromate.
$K_2O(CrO_3)_3$ $= K_2Cr_3O_{10}$, Potassium tri-chromate.
$K_2O(CrO_3)_4$ $= K_2Cr_4O_{13}$, Potassium tetra-chromate.
$(CaO)_3P_2O_5$ $= Ca_3(PO_4)_2$, Calcium tribasic phosphate.

(*c*) A **double salt** is a combination of **two salts.**

There are **three classes** of **double salts:**

1. Resulting from the union of **two simple salts.**

Example:

$(KCl)_2,PtCl_4$, potassium platinic chloride.

2. Resulting from the union of **two oxysalts.**

Example:

$K_2SO_4,Al_2(SO_4)_3 = K_2Al_2(SO_4)_4$, potassium aluminic sulphate. (Potash alum.)

3. Resulting from the union of a **simple salt** with an **oxysalt.**

Example:

$CaCl_2,CaCl_2O_2 = 2CaCl_2O$, calcium hypochlorite. (Bleaching lime.)

Laws Relating to Chemical Combination.

I. All **chemical compounds** are **definite** in their nature, and the ratio, by weight, of the elements composing a compound is constant.

Example: Water is composed of

Hydrogen, ...	11.11	per cent.
Oxygen, ...	88.89	"
	100.00	

This being established, then water must always be of that percentage composition.

The same elements, however, may unite in the same relative proportions by weight and produce entirely different compounds: *i. e.*, differing in their physical, chemical and physiological properties. Such compounds are termed **isomeric.**

Example: Oil of turpentine, oil of lemon and oil of copaiba are cômposed of the same elements in the same relative proportion by weight, namely, all three are composed of carbon and hydrogen in the proportion of 88.24 per cent. carbon and 11.76 per cent. hydrogen.

II. If an element enters into chemical combination with another in more than one proportion, these proportions will bear a definite ratio to each other.

Examples:

	Water.	Hydrogen Peroxide.		Carbon Monoxide.	Carbon Dioxide.						
H	1	1	C	3	3	N	7	7	7	7	7
O	8	16	O	4	8	O	4	8	12	16	20

	Mercurous Chloride.	Mercuric Chloride.		Methane.	Ethene.
Hg	100	100	C	75 (6)	85.7 (6)
Cl	17.75	35.5	H	25 (2)	14.3 (1)

Until 1804, compounds were expressed by their percentage composition.

Example:

$$\begin{aligned} H &= 11.11 \text{ per cent.} \\ O &= 88.89 \quad \text{"} \\ & \overline{100.00} \end{aligned}$$

Dalton, in 1804, observed the relation of the elements in the proportion of $\frac{2}{6}$ and $\frac{1}{6}$ in methane and ethene respectively, and concluded that it was proof of the existence of atoms. This was the beginning of the atomic theory.

III. **Dalton's Law**: The proportion by weight in which two or more elements enter into combination with any given

element, represents the proportion by weight in which these elements will unite in case they combine among themselves.

These combining proportions by weight of the elements are called **equivalent weights.**

Thus, the weights of two different elements, A and B, which combine with a third, C, represent the proportions in which they will themselves unite if union between them is possible, or they bear some simple relation to those proportions. Thus, 35.5 parts of chlorine and 80 parts of bromine combine with 23 parts of sodium. Then, according to the law, if chlorine could combine with bromine, 35.5 parts of the chlorine would be required for every 80 parts of the bromine.

IV. **Gay-Lussac's Law:** All the elements capable of being vaporized, when taken in the proportion of their equivalent weights, will occupy in the gaseous state the same volume as 1 part by weight of hydrogen, or ½ that volume. Sulphur, which is an exception, occupies in the gaseous state only ⅙ the volume of hydrogen, but when heated to 1000° C., it expands and occupies ½ the volume of hydrogen.

The law refers to chemical combination occurring in as definite proportions by volume as by weight.

1. Table of the Volume Occupied by the Equivalent Weights of the Elements in the Gaseous State, Corrected for 0° C. and 760 mm.

1 *grm.*	**hydrogen**	= 11.16 litres	equivalent volume 1.
14 *grms.*	nitrogen	= 11.16 "	
35.5 "	chlorine	= 11.16 "	
80 "	bromine	= 11.16 "	
127 "	iodine	= 11.16 "	
100 "	mercury	= 11.16 "	
56 "	cadmium	= 11.16 "	
8 "	oxygen	= 5.58 "	equivalent volume ½.
31 "	phosphorus	= 5.58 "	
75 "	arsenic	= 5.58 "	
16 "	sulphur	= 1.86 "	
16 "	" at 1000° C.	= 5.58 ".	

2. Volume Occupied by Compounds in the Gaseous State.

One-half the molecular weight.	9	grms.	water	= 11.16 litres.
	17	"	hydrogen sulphide .	= 11.16 "
	22	"	carbon dioxide . .	= 11.16 "
	37	"	ethyl ether	= 11.16 "
Once the molecular weight.	46	"	alcohol	= 22.32 "
	36.5	"	hydrochloric acid .	= 22.32 "
	17	"	ammoniacal gas . .	= 22.32 "

Relation of the Elements to Specific Heat.

Water has the greatest capacity for heat of all solids and liquids. Hydrogen has the greatest capacity for heat of all known substances. Uranium has the lowest capacity for heat of all known substances.

When the elements in the proportion of their equivalent weights are multiplied by their specific heat a simple relation will be shown to exist between them. The result of the multiplication is approximately 6.4 or one-half that number.

Thus, water taken as standard, 1.

	Specific Heat.	Equivalent Weight.
Lithium, ...	0.940 ×	7 = 6.58
Sodium, ...	0.293 ×	23 = 6.75
Potassium, ...	0.169 ×	39 = 6.61
Arsenic, ...	0.081 ×	75 = 6.11
Phosphorus, ...	0.212 ×	31 = 6.57
Mercury, ...	0.032 ×	100 = 3.20
Cadmium, ...	0.057 ×	56 = 3.20
Iron, ...	0.113 ×	28 = 3.18
Uranium, ...	0.027 ×	240 = 6.60

Uranium has the highest equivalent weight and the lowest specific heat of all the elements.

Equivalent weight is the least proportion by weight in which an element will enter into chemical combination with one part by weight of hydrogen.

Examples: 8 parts, by weight, of oxygen will enter into combination with 1 part, by weight, of hydrogen.

100 parts, by weight, of mercury, will enter into combination with 8 parts, by weight, of oxygen.

1. **Atomic weight according to specific gravity.**

The **atomic weight** of an element is its specific gravity in the gaseous state compared with hydrogen, with the exception of mercury and cadmium, in which the atomic weight is twice the specific gravity, and phosphorus and arsenic, in which the atomic weight is one-half the specific gravity.

Examples:

Atomic Weight.
Hydrogen, spec. grav. = 1.
Nitrogen, " " = 14. The atom of nitrogen weighs 14 times more than the atom of hydrogen.
Iodine, " " = 127. The atom of iodine weighs 127 times more than the atom of hydrogen.
Oxygen, " " = 16. The atom of oxygen weighs 16 times more than the atom of hydrogen.
Mercury, " " = 100, atomic weight = 200.
Cadmium, " " = 56 " " = 112.
Phosphorus, " " = 62 " " = 31.
Arsenic, " " = 150 " " = 75.

2. **Atomic weight according to specific heat or capacity for heat.**

The **atomic weight** of an element is that proportion by weight in which it is normal in regard to its capacity for heat. This definition has no exceptions.

By capacity for heat of an element, is understood the quantity of heat necessary to raise the temperature of a given **weight** of the element from 0° to 1° C. compared with the amount of heat necessary to increase the temperature of an **equal weight** of hydrogen through the same range. That part by **weight** of any element which will absorb the same amount of heat as will be absorbed by **one part** by weight of **hydrogen.**

Thus, since it requires 16 times more heat to raise the temperature of one gramme of **hydrogen** from 0° to 1° C. than to heat an equal weight (1 gramme) of **oxygen** through the same range, it follows that the capacity for heat of **hydrogen** is 16 times greater than that of **oxygen**: or, in other words, that the capacity for heat of **oxygen** is only $\frac{1}{16}$ that of **hydrogen.**

The proportion by weight in which an **element** is said to be **normal** in its capacity for heat, is that **proportion by weight** in which, on the application of a given amount of heat, the temperature will be increased to just the same extent as that produced by the same quantity of heat when applied to the heating of **one part by weight of hydrogen.**

Thus, if 16 parts by weight of **oxygen** and one part by weight of **hydrogen** be separately exposed to equal amounts of heat, the temperature of both substances will be increased equally; hence, 16 is the proportion by weight (H = 1) in which **oxygen** is **normal** in its capacity for heat.

3. The **atomic weight** of an element is represented by that number which, when multiplied by the element's capacity for heat, will give a product of about **6.4**. (See page 48.)

The **atomic volume** of an element is the volume of an element in the gaseous state, when taken in the proportion of its atomic weight, compared with the volume of one part by weight of hydrogen.

The atomic volume of all elements is 1, except mercury and cadmium, which is 2, and phosphorus and arsenic, which is $\frac{1}{2}$.

Examples:

1 grm. H = 11.16 litres, atomic volume = 1.
14 grms. N = 11.16 " " " = 1.
16 " O = 11.16 " " " = 1.

The **molecular weight** of an element or of a compound is a quantity by weight of the element, or compound, twice its specific gravity in the gaseous state compared with hydrogen.

Examples.

Elements: The specific gravity of N, in the gaseous state, compared with H is 14. Twice 14 = 28, the molecular weight of N.

The specific gravity of O, in the gaseous state, compared with H is 16. Twice 16 = 32, the molecular weight of O.

The specific gravity of Hg, in the gaseous state, compared with H is 100. Twice 100 = 200, the molecular weight of Hg (also the atomic weight).

The specific gravity of As, in the gaseous state, compared with H is 150. Twice 150 = 300, the molecular weight of As.

Examples.

Compounds: The specific gravity of water, in the gaseous state, compared with H is 9. Twice 9 = 18, the molecular weight of H_2O.

The specific gravity of carbon dioxide, in the gaseous state, compared with H is 22. Twice 22 = 44, the molecular weight of CO_2.

The specific gravity of acetic acid, in the gaseous state, compared with H is 30. Twice 30 = 60, the molecular weight of $C_2H_4O_2$.

It follows, therefore, that the **molecular weight** of an **element** or of a **compound** in the **gaseous state** occupies **twice** the **volume** occupied by one part by weight of hydrogen. This is known as the **molecular volume** of an element or of a compound.

Thus,

1 grm.	**hydrogen**	**occupies**	11.16	**litres,**	atomic	vol.
2 grms.	"	occupy	22.32	"	molecular	"
28 "	nitrogen	"	22.32	"	"	"
71 "	chlorine	"	22.32	"	"	"
18 "	water	"	22.32	"	"	"
44 "	carbon dioxide	"	22.32	"	"	"
34 "	hydrogen peroxide	"	22.32	"	"	"

The **molecular volume** of an element or of a compound is a volume of the element or compound in the gaseous state twice the volume of the atom of hydrogen.

The molecular volume of elements and of compounds is 2.

	Equiv. Wt.	At. Wt.	Molec. Wt.	At. Vol.	Molec. Vol.
H =	1	1	2	1	2
O =	8	16	32	1	2
N =	14	14	28	1	2
Hg =	100	200	200	2	2
As =	75	75	300	½	2

VALENCE (Atomicity, Quantivalence, Equivalence).

The elements combining in the proportion of their atomic weight possess different saturating powers. The saturating power is referred to hydrogen as unity.

Examples;

$$HCl + Na = NaCl + H.$$

The saturating power of Na is equivalent to one atom of H.

$$2HCl + Ca = CaCl_2 + H_2.$$

The saturating power of Ca is equivalent to two atoms of H.

$$3HCl + Au = AuCl_3 + H_3.$$

The saturating power of Au is equivalent to three atoms of H.

$$4HCl + Pt = PtCl_4 + H_4.$$

The saturating power of Pt is equivalent to four atoms of H.

The elements are arranged, according to their saturating power, into six groups:

Monads, as H, Na, Ag.
Diads, " O, Ba, Sr.
Triads, " Bi, Sb, N.
Tetrads, " C, Sn, Pt.
Pentads, " Ta, V.
Hexads, " Ur, Mo.

Those elements having an **even** valence, as 2, 4, 6, are termed **artiads**, and those having an **uneven** valence, as 1, 3, 5, are termed **perissads.**

The **combining proportion** of a compound is always equal to the sum of the atomic weights of its molecular constituents.

Example:

Molecular weight of $H_2O = 18$.

When water enters into combination, it does so always in the proportion of its molecular weight or a multiple or submultiple of that number.

Na_2O	$= 62$	molec. wt.	electro-positive compounds.
MgO	$= 40$	" "	
FeO	$= 72$	" "	
HCl	$= 36.5$	" "	electro-negative compounds.
CO_2	$= 44$	" "	
H_2SO_4	$= 98$	" "	

These numbers are made use of in calculating the quantity of different substances required in preparing exact quantities of chemical compounds.

Examples:

Molec. Wt. 62.		Molec. Wt. 44.		Molec. Wt. 106.
Na_2O	+	CO_2	=	Na_2CO_3.

62 parts of Na_2O and 44 parts of CO_2 are required to form 106 parts of Na_2CO_3.

Molec. Wt. 72.		Molec. Wt. 98.		Molec. Wt. 152.		
FeO	+	H_2SO_4	=	$FeSO_4$	+	H_2O.

To prepare ferrous sulphate, $FeSO_4$, 72 parts, by weight, of FeO and 98 parts, by weight, of H_2SO_4 are required to produce 152 parts of the sulphate. If an excess of the acid be employed, another compound of iron, ferric sulphate, $Fe_2(SO_4)_3$ will be formed.

Twice the molecular weight, or 73 parts, by weight, of HCl are equivalent in saturating power to 98 parts, by weight, of H_2SO_4. Therefore, a given weight of a chloride may contain more of the positive element than the same weight of a sulphate of the same positive element.

Example: 10 grammes of strychnine chloride contain more strychnine than 10 grammes of strychnine sulphate. Thus, 10 grammes of the chloride, $C_{21}H_{22}N_2O_2$ HCl, contain 9.01 grammes of strychnine, while 10 grammes of the sulphate, $(C_{21}H_{22}N_2O_2)_2$ $H_2SO_4,7H_2O$, contain 7.48 grammes strychnine.

Molec. Wt. Strychnine Chloride.		Molec. Wt. Strychnine.		Grammes Strychnine Chloride.		Grammes Strychnine.
370.5	:	334	::	10	:	9.01

Molec. Wt. Strychnine Sulphate.		Twice the Molec. Wt. Strychnine.		Grammes Strychnine Sulphate.		Grammes Strychnine.
892	:	668	::	10	:	7.48

METHODS OF ANALYSIS OF INORGANIC COMPOUNDS, AND THE EXPRESSION OF THEIR COMPOSITION BY FORMULÆ.

Analysis.—(*a*) **Qualitative:** The determination of the elements entering into the composition of the compound.

(*b*) **Quantitative:** The determination of the **quantity** of each element entering into the composition of the compound.

Method of deducing formulæ from the results of a quantitative analysis: 1. Suppose, by qualitative analysis, a certain compound is found to be composed of Fe and SO_4.

A given weight of the compound is dissolved in water, and the iron precipitated by $(NH_4)_2S$ as sulphide, FeS, which is collected on a filter, washed, dried and weighed. The sulphuric acid in the filtrate is precipitated by $BaCl_2$ as $BaSO_4$, which latter is also collected on a filter, washed, dried and weighed.

Then,

$\overset{\text{Molec. Wt. FeS.}}{88} : \overset{\text{Atomic Wt. Fe.}}{56} ::$ wt. of prec. of FeS : $x =$ the quantity of Fe.

And

$\overset{\text{Molec. Wt. BaSO}_4\text{.}}{233} : \overset{\text{Molec. Wt. SO}_4\text{.}}{96} ::$ wt. of prec. of $BaSO_4$: $x =$ the quantity of SO_4.

2. To deduce a formula from the above results, employ the following rule:

As the quantity of the positive element or radical is to the quantity of the negative element or radical, so is the atomic weight or the molecular weight of the positive element or radical to **x** = the quantity of the negative element or radical. Divide **x** by the atomic weight of the element or the molecular weight of the compound implied.

Examples:

(*a*) 10 parts of a substance furnished.

Fe, ... 3.684 parts.
SO_4, ... 6.316 "

Then,

$$3.684 : 6.316 :: \overset{\text{Atomic Wt. Fe.}}{56} : \overset{\text{Molec. Wt. SO}_4\text{.}}{96} \div 96 = 1 \ (SO_4),$$

i. e., there are in combination with 56 parts of iron (once the atomic weight of Fe) 96 parts of SO_4 (once the molecular weight of SO_4), therefore the formula for the compound is $FeSO_4$, ferrous sulphate.

(*b*) 10 parts of a substance furnished.

Fe, ... 2.8 parts.
SO_4, ... 7.2 "

Then,

$$2.8 : 7.2 :: \overset{\text{Atomic Wt. Fe.}}{56} : 144 \div \overset{\text{Molec. Wt. } SO_4.}{96} = 1.5 \ (SO_4),$$

i. e., there are in combination with 56 parts of iron (once the atomic weight of Fe) one and one half times the molecular weight of SO_4. As a half molecule is not admissible, the formula must be $Fe_2(SO_4)_3$, ferric sulphate.

(*c*) 953 parts of a substance containing water of crystallization furnished.

$$\left.\begin{array}{lll} Na_2O & 206 & \text{parts.} \\ CO_2 & 147 & \text{"} \end{array}\right\} = 353 \text{ parts.} \qquad \text{Molecular wt. of } Na_2O = 62.$$
$$\begin{array}{lll} H_2O & 600 & \text{"} \end{array} \qquad\qquad \text{"} \quad \text{"} \quad CO_2 = 44.$$

Then,

$$206 : 147 :: \overset{\text{Molec. Wt. } Na_2O.}{62} : 44.2 \div \overset{\text{Molec. Wt. } CO_2.}{44} = 1 \ (CO_2),$$

therefore the formula is Na_2CO_3, and

$$\overset{\text{Quant. } H_2O.}{353} : 600 :: \overset{\text{Molec. Wt. } Na_2CO_3.}{106} : 180.1 \div \overset{\text{Molec. Wt. } H_2O.}{18} = 10 \ (H_2O),$$

i. e., for one molecule of Na_2CO_3 there are 10 molecules of H_2O, therefore the formula of the compound is $Na_2CO_3 + 10H_2O$, sodium carbonate.

Miscellaneous Examples in Stoichiometry.

1. How much Fe in 10 grammes FeS?

$$\overset{\text{Molec. Wt. FeS.}}{88} : \overset{\text{Atomic Wt. Fe.}}{56} :: 10 : x = \text{quantity of Fe.}$$

2. How much sulphide of iron (FeS) may be prepared from 10 grammes Fe?

$$\overset{\text{Atomic Wt. Fe.}}{56} : \overset{\text{Molec. Wt. FeS.}}{88} :: 10 : x = \text{quantity of FeS.}$$

3. How much H_2S **by volume** may be obtained from 10 grammes FeS?

88 grammes FeS (once molecular weight) will furnish 22.32 litres of H_2S.

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

$$88 : 22.32 :: 10 : x = \text{quantity by volume of } H_2S.$$

4. How much H_2S **by weight** may be obtained from 15 grammes FeS?

88 grammes FeS (once molecular weight) will furnish 34 grammes of H_2S.

Molec. Wt. H_2S.

88 : 34 :: 15 : x = quantity by weight of H_2S.

5. How much oxygen **by volume** may be obtained from 20 grammes $KClO_3$?

$$KClO_3 = KCl + O_3.$$

Molecular weight of $KClO_3 = 122.6$.

Atomic weight of $O = 16$.

One molecule of $KClO_3$ will furnish three atoms of O.

Once the atomic weight (16) of oxygen in grammes will occupy 11.16 litres.

3 × 11.16 = 33.48 litres, consequently one molecule, in grammes (122.6 grammes.) $KClO_3$ will furnish 33.48 litres or 33480 c.c. oxygen.

122.6 : 33480 :: 20 : x = number of c.c. oxygen furnished.

6. How much hydrogen sulphide **by volume** will be required to precipitate 12 grammes As_2O_3 as As_2S_3?

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

The molecular weight of As_2O_3 is 198.

" " " of H_2S is 34.

Three molecules of H_2S are required to precipitate one molecule of As_2O_3.

1 molecule, expressed in grammes, or 34 grammes of H_2S measures 22.32 litres; 3 molecules = 3 × 22.32 = 66.96 litres or 66960 c.c.

198 : 66960 :: 12 : x = number of c.c. H_2S required.

7. How much hydrogen sulphide by weight will be required to precipitate 12 grammes of As_2O_3 as As_2S_3?

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

Molecular weight of $As_2O_3 = 198$.

" " of $H_2S = 34$.

Three molecules of H_2S are required to precipitate one molecule of As_2O_3, consequently $3 \times 34 = 102$ grammes H_2S are required to precipitate 198 grammes As_2O_3.

$$198 : 102 :: 12 : x = \text{quantity by weight of } H_2S.$$

8. How much As_2O_3 are 15 grammes As_2S_3 equal to?

$$\overset{\substack{\text{Molec. Wt.} \\ As_2S_3}}{246} : \overset{\substack{\text{Molec. Wt.} \\ As_2O_3}}{198} :: 15 : x = \text{quantity by weight of } As_2O_3.$$

OXYGEN.

Symbol, O; atomic weight, 16; atomic volume, 1; molecular weight, 32; molecular volume, 2; equivalent weight, 8; specific gravity compared with air, 1.1056; 16 grammes oxygen at 0° C. and 760 millimetres measure the same volume as 1 gramme hydrogen, namely, 11.16 litres; 1 litre at 0° C. and 760 millimetres weighs 1.433 grammes; 100 cubic inches at 60° F. and 30 inches pressure weigh 34.27 grains; 16 grains measure 46.66 cubic inches.

History: Discovered August 1, 1774, by Priestley, who called it "Dephlogisticated air." In 1775 Scheele, of Sweden, independently of Priestley, discovered it, and called it "Empyreal air." Condorcet studied it in 1777, and named it "Vital air." Lavoisier in 1778 named it oxygen, or acid-begetter, because of his belief of its entering into the composition of all acids and constituting their acidifying principle.

Natural history: Oxygen is the most abundant and most widely distributed of all the elements. Except in atmospheric air, it is always found in a combined state.

It is found in the three kingdoms: mineral, vegetable and animal.

Nearly $\frac{3}{4}$ of all terrestrial matter is oxygen.

About $\frac{1}{2}$ of the solid crust of the earth is oxygen.

$\frac{8}{9}$ of water is oxygen.

$\frac{1}{5}$ by volume of the air is oxygen.

48 per cent. of calcium carbonate, $CaCO_3$ (limestone), about 48 per cent. of aluminic oxide, Al_2O_3 (clay), and about 53 per

cent. of silica (SiO_2), (the three chief constituents of the earth's crust), is oxygen.

About $\frac{1}{4}$ of all growing vegetable matter is water, $\frac{8}{9}$ of which is oxygen.

It is a constituent of organic compounds, as glucose, $C_6H_{12}O_6$, starch, $C_6H_{10}O_5$, urea, $CO(NH_2)_2$, etc.

All organic compounds do not contain oxygen; probably the great majority of them contain oxygen.

About 75 per cent. of the tissues of living animals is water, $\frac{8}{9}$ of which is oxygen.

Preparation of oxygen: 1. It was first obtained (by Priestley) by heating, and thereby decomposing, mercuric oxide, HgO (red oxide of mercury), into its ultimate elements, mercury and oxygen. The oxygen is evolved as a gas, and the mercury remains in the metallic state:

$$HgO = Hg + O.$$

How much oxygen by **weight** may be obtained from—for example, 15 grammes of HgO?

The molecular weight of HgO is 216.

Every 216 parts of HgO will evolve 16 parts of O:

$$\begin{array}{ccccccc} \text{Molec. Wt. HgO.} & & \text{Atomic Wt. O.} & & & & \\ 216 & : & 16 & :: & 15 & : & x = \text{weight of O.} \end{array}$$

How much oxygen by **volume** may be obtained from—for example, 15 grammes HgO?

Every 216 grammes of HgO will evolve 16 grammes oxygen.

16 grammes oxygen measure 11.16 litres (11160 c.c.).

$$\begin{array}{ccccccc} \text{Molec. Wt. HgO.} & & & & \text{Cubic Centimetres.} & & \\ 216 & : & 15 & :: & 11116 & : & x = \text{volume of O.} \end{array}$$

2. By decomposing manganese dioxide, MnO_2, by heat.

$$2MnO_2 = Mn_2O_3 + O,$$

or at higher temperature,

$$3MnO_2 = Mn_3O_4 + O_2.$$

3. By heating manganese dioxide, MnO_2, with sulphuric acid.

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

4. By gently heating potassium bichromate, $K_2Cr_2O_7$, with sulphuric acid.

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + O_3.$$

5. By heating potassium chlorate, $KClO_3$. The $KClO_3$ before being heated is usually mixed with an inert substance, as MnO_2, to moderate the violence of decomposition of the chlorate. The decomposition is effected in a copper or an iron retort.

$$2KClO_3 = KClO_4 + KCl + O_2.$$

At a higher temperature, the potassium perchlorate, $KClO_4$, is decomposed.

$$KClO_4 = KCl + O_4.$$

The reaction is usually expressed,

$$KClO_3 = KCl + O_3.$$

6. By heating potassium nitrate,

$$KNO_3 = \overset{\text{Potass. Nitrite.}}{KNO_2} + O.$$

If the KNO_3 be heated at a high temperature the KNO_2 produced is decomposed, with the evolution of nitrogen and oxygen.

7. By bringing sulphuric acid in contact with metallic platinum at a high temperature.

$$H_2SO_4 = H_2O + SO_2 + O.$$

8. By heating barium dioxide, BaO_2 (peroxide).

Barium monoxide, BaO, when gently heated in the presence of air, takes up oxygen, with the formation of barium dioxide, BaO_2. The latter compound when strongly heated gives up one atom of oxygen.

$$BaO_2 = BaO + O.$$

By gently heating (in contact with air) the barium monoxide, BaO, produced as an end product in the foregoing reaction, it takes up oxygen again, forming barium dioxide, BaO_2, which when strongly heated gives up oxygen, as in the reaction just given, thus making the preparation of oxygen by this method practically continuous.

9. Pure oxygen may be obtained by the electrolytic decomposition of H_2O.

By the action of leaves of plants in sunlight on carbon dioxide, the carbon is fixed, and oxygen is set free.

Properties: It is a colorless, odorless, tasteless gas. Density, 16 times that of hydrogen. Sparingly soluble in water. Water will hold in solution 3 to 4 per cent. of oxygen. The lower the temperature of water, the higher its solvent power for oxygen, and the higher the temperature, the lower its solvent power for the gas.

It was liquefied by Pictet, in 1877, by exposing it to a temperature of —100° C. and a pressure of 300 atmospheres. Afterward it was found that it would become liquid at —118° C. and a pressure of 50 atmospheres. Oxygen boils at a temperature of —225° C.

Oxygen is a supporter of combustion, but not combustible.

Examples: A spark brought into an atmosphere of oxygen bursts into flame. This property is possessed by only one other gas, viz., hyponitrous oxide, N_2O.

Sulphur burns more rapidly in an atmosphere of oxygen than in air (sulphurous anhydride, SO_2, being formed).

Lighted charcoal (carbon) burns more rapidly in oxygen than in air (carbon dioxide being produced).

Ignited phosphorus burns in oxygen with increased vigor, forming phosphoric anhydride, P_2O_5.

Certain substances which ordinarily undergo very slow oxidation in air, oxidize very rapidly in an atmosphere of oxygen; for instance, hot metallic iron (a watch spring), when brought into an atmosphere of oxygen, burns (oxidizes) with great vigor, with the production of ferric oxide, Fe_2O_3.

Physiological properties: Oxygen is absolutely necessary to sustain animal life. It enters into combination with the coloring matter of the blood, hæmoglobin, $C_{636}H_{1025}N_{164}O_{181}FeS_3$, to form oxyhæmoglobin, $C_{636}H_{1025}N_{164}O_{181}FeS_3O_2$ (molecular weight, 14,161). The oxygen thus combined in oxyhæmoglobin is in rather feeble combination, and is readily given up in the organism in the process of oxidation. Thus, arterial blood contains oxyhæmoglobin which, in its passage from the capillary blood-vessels through the tissues, gives up its oxygen,

is reduced, and appears in venous blood as hæmoglobin, which again in the lungs combines with oxygen, to form oxyhæmoglobin, is reduced in the tissues, and appears in the venous blood as hæmoglobin, thus completing a cycle in carrying oxygen to satisfy the needs of the organism.

The oxygen combined with hæmoglobin as oxyhæmoglobin is easily displaced by carbon monoxide to form carbonic oxide hæmoglobin, $C_{636}H_{1025}N_{164}O_{189}FeS_3CO$, molecular weight 14,157. In short, hæmoglobin has a greater affinity for carbon monoxide than it has for oxygen, and when a mixture of the two gases is inhaled the hæmoglobin will, in preference, combine with the carbon monoxide.

Carbonic oxide hæmoglobin in its passage from the arterial system through the tissues to the venous system does not give up its carbon monoxide, but is returned to the lungs as carbonic oxide hæmoglobin. On continuously inhaling an atmosphere containing carbon monoxide a time arrives when the hæmoglobin in the blood is largely or almost wholly in combination with carbon monoxide, the quantity of oxygen carried by any remaining hæmoglobin as oxyhæmoglobin is insufficient for the needs of the organism, and consequently death ensues. This is the chemical explanation of death by carbonic oxide poisoning. (Carbonic oxide is contained in the gases emanating from lime-kilns in the process of burning lime, and is also largely contained in the illuminant called "water gas.") The red color of arterial blood is due to oxyhæmoglobin, the purple-red color of venous blood is due to hæmoglobin (sometimes called reduced hæmoglobin). Blood containing carbonic oxide hæmoglobin is rose-red in color.

Hæmoglobin, oxyhæmoglobin, carbonic oxide hæmoglobin and methæmoglobin are definite crystalline chemical compounds. They are readily distinguished spectroscopically by the difference in their spectra.

The presence of oxygen and of carbon dioxide in blood may be determined by withdrawing the gases from the blood contained in a bulb, by means of Hüfner's modification of Sprengel's pump, and collecting them in a eudiometer. On introducing a solution of barium hydroxide into the eudiometer the liquid will become turbid, due to the formation of barium carbonate, thus indicating the presence of carbon dioxide. On introducing a solution of pyrogallic acid and afterward a piece of caustic soda into the same eudiometer, the liquid will become black, due to the action of the oxygen in the eudiometer on the alkaline solution of pyrogallic acid. The gas in the eudiometer will be almost entirely absorbed by the barium hydroxide and alkaline pyrogallic acid solutions; any gas remaining unabsorbed is nitrogen, which, in small quantity, is one of the constituents of the gases of the blood.

Carbon Dioxide, CO_2, is a normal constituent of the air. It is contained in the air in the proportion of from 2 to 4 parts in 10,000 of air (0.02 to 0.04 per cent.). Air containing 0.1 per cent. of CO_2 (10 parts in 10,000) is unfit for respiration. In stating that the limit of contamination of air with CO_2 is 0.1 per cent., it is understood that the CO_2 is derived from the breath. This percentage of CO_2 may be looked upon simply as an index of the quantity of other substances which are poisonous (possibly of the nature of volatile ptomaines), and which are derived from the breath, as air containing only 0.1 per cent. of CO_2, derived from sources outside of the animal body may be breathed without discomfort. Carbon dioxide is exhaled by animals, and also results from the combustion of carbonaceous substances. Plants in sunlight break up CO_2, appropriating the carbon and setting free the oxygen.

$$6CO_2 + 5H_2O = \overset{\text{Cellulose.}}{C_6H_{10}O_5} + 6O_2.$$

The quantity of oxygen consumed per day by 9 ounces of carbon (given off as CO_2) and ½ ounce (0.5 ounce) of hydrogen (given off as H_2O) of the food taken by the average man, is 28 ounces.

$$C + O_2 = CO_2.$$

Atomic Wt. C.		Twice Atomic Wt. O.		Oz. C.		Oz. O.
12	:	32	::	9	:	24

$$H_2 + O = H_2O.$$

Twice Atomic Wt. H.		Atomic Wt. O		Oz. H.		Oz. O.
2	:	16	::	0.5	:	4

28 oz. oxygen.

The 9 ounces of carbon expired per day as CO_2, is equivalent to the expiration of 1240 cubic inches of CO_2 per hour.

The 9 ounces of carbon and ½ ounce of hydrogen consume 28 ounces of oxygen per day, or 1500 cubic inches per hour, and to furnish 1500 cubic inches of oxygen, 7500 cubic inches of air are required.

The 1240 cubic inches CO_2 expired in one hour is sufficient to contaminate 1,240,000 cubic inches of air with CO_2 to the extent of 0.1 per cent., which is the generally acknowledged limit of permissible pollution.

$1240 \times 1000 = 1{,}240{,}000$ cubic inches of air polluted with CO_2 to the extent of 0.1 per cent.

7500 cubic inches of air are required to furnish sufficient oxygen to produce 1240 cubic inches of CO_2.

Therefore, the quantity of air used plus the quantity of air vitiated per hour is

$7500 + 1{,}240{,}000 = 1{,}247{,}500$ cubic inches of air or about 721 cubic feet of air vitiated to the extent of 0.1 per cent. of CO_2 per hour.

It follows that the quantity of air required for respiration by an ordinary man is equal to that contained in a room 9 feet square and 9 feet high, renewed every hour, *i. e.*, 721 cubic feet.

Table of Oxygen Consumed and Air Vitiated by Combustion.

12 Candle-Power.	O Consumed.	CO_2 Produced.	Air Vitiated to the extent of 0.1 per cent. CO_2.
Illuminating gas	5.45 cubic feet	3 21 cubic feet	3482.5 cubic feet
Sperm oil	4.75 " "	3.33 " "	3567.5 " "
" candle	7.57 " "	5.77 " "	6148.5 " "
Wax "	8.41 " "	5.90 " "	6322.5 " "
Tallow "	12.00 " "	8.73 " "	9330 0 " "

One candle-power is equivalent to the light furnished by a pure sperm candle, which in burning consumes sperm at the rate of 2 grains per minute.

Chemical properties: Oxygen is a supporter of combustion, but is not itself combustible. It is the type of the electro-negative elements, and combines with all the elements except fluorine.

It may be detected qualitatively: (*a*) By its being a supporter of combustion, but hyponitrous oxide, N_2O, is also a supporter of combustion. Oxygen may be distinguished from hyponitrous oxide by mixing the gas in question with nitrogen protoxide, N_2O_2. The latter gas when brought in contact with oxygen will produce red-brown fumes of N_2O_3 or of N_2O_4. No change takes place when N_2O_2 is brought in contact with hyponitrous oxide.

(*b*) Water is formed when an electric spark is passed through a mixture composed of one volume of oxygen and two volumes of hydrogen.

OZONE.

Molecular formula of ozone, O_3. Molecular volume, 2. Specific gravity compared with hydrogen, 24. Molecular weight, 48.

O_2 represents the molecule of oxygen.

O_3 represents the molecule of ozone.

Ozone is considered to be an allotropic condition of oxygen in which three volumes are condensed into two, one of the volumes being in a different electrical condition from the other two volumes. One of the atoms is looked upon as being in the positive condition, and the other two as negative, thus;

$$\overset{-}{O}\overset{+}{O}\overset{-}{O}$$

History: Von Marum, in 1785, noticed that when an electric current was passed through oxygen a peculiar odor was produced, which somewhat resembled that observed after a stroke of lightning and sometimes called "sulphurous."

In 1840, Schoenbein noticed the similarity between the odor thus produced and the odor observed in the electrolysis of water and in the slow oxidation of phosphorus and sulphur, and found that in each case the substance produced turned paper moistened with a solution of potassium iodide and starch decidedly blue.

During the same year, Marignac demonstrated that the substance produced was an allotropic modification of oxygen.

Simultaneously with the production of ozone, a compound termed antozone was produced, and was represented by the formula $O_3 = \overset{+}{O}\,\overset{-}{O}\,\overset{+}{O}$, in which one of the atoms of oxygen was looked upon as being in the negative and two atoms in the positive condition. It was afterward shown that this compound was hydrogen peroxide, H_2O_2.

$$O_2 + O_2 + H_2O = H_2O_2 + O_3.$$

Preparation of Ozone; 1. By **electrical agency.** The silent discharge of electricity in moist oxygen.

2. By **slow combustion.**

(*a*) The slow oxidation of phosphorus in moist air.

(*b*) The slow oxidation of ether, viz., the placing of a hot glass rod in a vessel containing vapor of ether.

Properties of Ozone: A colorless gas possessing a phosphorus-like odor. It is probably always present in the air in minute quantity, except in the air of large cities, where it is decomposed. As it is one of the results of the slow oxidation of oils, especially of turpentine, it is, therefore, found in larger quantity in the air of pine forests. It is found in the air, especially after a thunder-storm. It possesses, to a marked degree, the property of oxidizing and destroying impurities in air.

It is a powerful oxidizing agent and is also a reducing agent.

It oxidizes As_2O_3 to As_2O_5.
" Ag " Ag_2O.
" Hg " HgO.

In these cases the ozone, O_3, gives up one atom of oxygen, the other two atoms remaining as ordinary oxygen.

$$As_2O_3 + 2O_3 = As_2O_5 + 2O_2.$$
$$Hg + O_3 = HgO + O_2.$$

It decomposes potassium iodide, oxidizing the potassium and liberating the iodine.

$$2KI + O_3 + H_2O = 2KOH + O_2 + I_2.$$

Tests for Ozone: Ozone in contact with paper moistened with a solution of potassium iodide and starch sets the iodine free, which latter acting on the starch turns it blue. Hydrogen peroxide, H_2O_2, responds to the test in a similar manner, as also does nitrous acid, HNO_2. The solution employed to moisten the paper is prepared by dissolving 1 part of potassium iodide and 5 parts of starch in 100 parts of water.

Ozone may be distinguished from hydrogen peroxide by its action on a polished surface of metallic silver. Ozone produces a blue-black stain on the silver; hydrogen peroxide has no action.

HYDROGEN.

Atomic weight, 1. Molecular weight, 2. Molecular volume, 2. Specific gravity compared with air, 0.0693 (14.44 times lighter than air).

1 gramme of hydrogen at 0° C. and 760 millimetres pressure measures 11.16 litres.

1 grain of hydrogen at 60° F. and 30 inches pressure measures 46.66 cubic inches.

100 cubic inches weigh 2.14 grains.

1 litre weighs 0.0896 gramme (1 crith).

If the specific gravity (compared with hydrogen) of an element, or a compound in the gaseous state, be multiplied by 0.0896, the resultant is the weight of one litre of the substance in the gaseous state.

Example:

Molecular weight of CO_2 is 44.

Specific gravity of CO_2 compared with hydrogen is 22.

$0.0896 \times 22 = 1.9712$ gramme, the weight of 1 litre of CO_2.

Special history: A gas, which is now known to have been hydrogen, was recognized by Boyle in 1672.

Cavendish obtained it in 1776, and called it **inflammable air.**

Because of water being produced when the gas was burned, Lavoisier named it **hydrogen.**

Natural history: It is found in the three kingdoms—**mineral, vegetable** and **animal.**

In the **mineral kingdom** it is found free in volcanic gases and in the "fire-damp" of coal mines. It is present in the air, not, however, in the free state, but in combination as vapor of water. In combination with oxygen it forms $\frac{1}{9}$ part by weight of water. It occurs in various mineral substances in combination with oxygen as water of hydration.

In the **vegetable kingdom** it is found as a constituent of all tissues, as well as in the water with which the tissues are associated. It is a constituent of most of the organic compounds of vegetable origin, as $C_6H_{12}O_6$, glucose, $C_6H_{10}O_5$, cellulose, starch.

In the **animal kingdom** it is a constant constituent of the tissues, and is also a constituent of most organic compounds of animal origin, as $CO(NH_2)_2$, urea.

Preparation of Hydrogen: 1. By decomposing water by means of intense heat.

2. By decomposing water with metallic potassium or sodium.

$$K + H_2O = KOH + H.$$

In this decomposition sufficient heat is evolved to ignite the hydrogen in the presence of the oxygen of the air. Combination of the two elements takes place, with the formation of water.

To obtain hydrogen by this method, the decomposition must be performed out of contact with free oxygen, in an inverted jar filled with water.

3. By decomposing water with a current of electricity (by electrolysis).

$$H_2O = H_2 + O.$$

4. By decomposing water by bringing it, in the form of steam, in contact with certain metals heated to a red heat, such as red-hot iron.

$$Fe_3 + 4H_2O = Fe_3O_4 + 4H_2.$$

5. By passing steam over red-hot coke or charcoal.

$$C + 2H_2O = CO_2 + 2H_2.$$

6. By decomposing sulphuric acid with metallic zinc.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

7. By decomposing sulphuric acid with metallic iron.

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

8. By decomposing hydrochloric acid with metallic zinc.

$$Zn + 2HCl = ZnCl_2 + H_2.$$

9. By decomposing hydrochloric acid with metallic iron.

$$Fe + 2HCl = FeCl_2 + H_2.$$

Hydrogen is generally prepared by the action of zinc on dilute sulphuric acid. Prepared in this manner it may contain hydrogen sulphide, or hydrogen arsenide, derived from impurities in the zinc. The hydrogen may be purified by passing it through two Woulff's bottles containing solutions of sodium hydroxide and argentic nitrate respectively.

How much hydrogen by volume may be obtained from 15 grammes sulphuric acid?

The molecular weight of H_2SO_4 is 98.

Every molecule of H_2SO_4 contains 2 atoms of H.

One atom of H, expressed in grammes, will occupy a volume of 11.16 litres. Two atoms of hydrogen in grammes will measure 22.32 litres, consequently from one molecule (expressed in grammes) or 98 grammes of H_2SO_4 there are evolved 22.32 litres of hydrogen; therefore,

$98 : 15 :: 22.32 : x =$ volume of H from 15 grammes H_2SO_4.

Physical properties: When pure, a colorless, tasteless, odorless gas. It is soluble in water, at a temperature of from 0° C. to 20° C., to the extent of about 1.9 per cent. by volume. The coefficient of absorption of hydrogen by water is 0.019.

Subjected to a pressure of 3000 atmospheres at ordinary temperature it still remains a gas, but at a temperature of —180° C. it may be liquefied by a pressure of 99 atmospheres. If the pressure, while in the liquid state, be removed, it boils and forms a solid.

It is the lightest substance known, being 240,000 times lighter than hammered iridium, the heaviest substance known. Volume for volume, it is 14.44 times lighter than air, and on this account has been used for filling balloons.

Knowing that hydrogen is 14.44 times lighter than air, the specific gravity of gaseous substances, compared with air, may readily be calculated, if their specific gravity compared with hydrogen be known, by dividing their specific gravity compared with hydrogen by 14.44.

Example: CO_2 molecular weight is 44. Specific gravity compared with H is 22. Then, $22 \div 14.44 = 1.524$, specific gravity of CO_2 compared with air.

The specific gravity of a gaseous substance compared with air may be found compared with hydrogen by multiplying the specific gravity of the gaseous substance compared with air by 14.44.

Hydrogen possesses to a marked degree the power of diffusion. In diffusion, gases follow the law that **the rate of diffusion of two gases is inversely as the square roots of the densities of the gases.** Hydrogen diffuses 3.8 times more rapidly than air, *i. e.*, if hydrogen be placed in a tube, one end of which is closed with a porous diaphragm of plaster-of-Paris and the other end immersed in water, the hydrogen will diffuse through the diaphragm and air will enter, but for every 1 c.c. of air which enters, 3.8 c.c. of hydrogen escape.

Physiological effects: It is in itself not poisonous, but if breathed alone continuously death results from absence of oxygen.

Chemical properties: When pure, it is an odorless, colorless, tasteless gas.

It is an electro-positive, monivalent element.

It is not a supporter of combustion, but is combustible. When pure, it burns with a colorless flame, producing great heat. When burned with a sufficiency of oxygen, more heat is produced than in the combustion of an equal volume of any other known substance. One gramme of hydrogen when burned with an adequate quantity of oxygen will produce sufficient heat to raise the temperature of 34,462 grammes of water from 0° C. to 1° C.

The intense heat produced in the combustion of hydrogen with oxygen is made available by the oxyhydrogen blowpipe, a contrivance in which hydrogen and oxygen are brought together from separate orifices and the mixture ignited.

Hydrogen does not combine with oxygen under ordinary conditions, but when a direct flame is applied to a mixture of the two gases, or when the mixture is fired by an electric spark, combination takes place with explosive violence.

When a jet of hydrogen is brought in contact with spongy platinum, combination is effected with oxygen and the jet of hydrogen is ignited. (Principle of Doebereiner's lamp.)

Compounds of Hydrogen and Oxygen.

There are only **two** compounds of hydrogen with oxygen, namely,

H_2O, Hydrogen monoxide (water).

H_2O_2, Hydrogen peroxide.

Water, H_2O (Hydrogen Monoxide).

Molecular weight of water, 18. Specific gravity compared with hydrogen, 9.

18 grammes of vapor of water measure 22.32 litres.

18 c.c. water = 22320 c.c. steam, at 0° C. and 760 millimetres.
1 c.c. " = 1240 c.c. " " " "

i. e., one volume of water will make 1240 volumes of steam measured at 0° C. and 760 millimetres.

273 : 373 :: 1240 : 1694 = volumes of steam measured at 100° C. evolved from one volume of water.

Percentage composition of water.

Hydrogen, ...	11.14	per cent.
Oxygen, ...	88.86	"
	100.00	

Special history of water: It was regarded by the ancients as one of the four elements.

Priestley suspected its composition in 1780. Dr. Watt confirmed Priestley's suspicion, and wrote to Dr. Priestley, April 6, 1783, that water was a compound of dephlogisticated air and inflammable air.

Natural history: It is found in nature in rain, snow, hail, and in rivers and seas. A large percentage of animal and vegetable structures is water. It is found combined in many minerals as water of hydration.

The quantity of water in the world is sufficient to cover the earth's surface to the depth of one mile.

Preparation of water: By burning hydrogen in oxygen, or by passing an electric spark through a mixture of two volumes of hydrogen and one volume of oxygen.

Determination of the composition of water: 1. **By analysis,** *i. e.*, the resolving of the compound into its elementary constituents.

2. **By synthesis,** *i. e.*, producing the compound from its constituents.

In the analytical method, water slightly acidulated with sulphuric acid to increase its conductivity, is decomposed in an appropriate two-armed eudiometer by means of a current of electricity. Hydrogen is evolved from the water around the negative platinum electrode, oxygen at the positive platinum electrode. Two volumes of hydrogen will collect in one arm of the eudiometer and one volume of oxygen in the other. The quantity of oxygen appearing in the eudiometer is slightly less than the required volume, due to the somewhat greater solubility of oxygen in water than hydrogen, and also because of some of the oxygen being ozonized, with a consequent condensation of volume.

The gas evolved from the negative electrode may be shown to be hydrogen by burning when ignited, and the production of water as a result of the combustion. Oxygen may be recognized by its vigorously supporting combustion and turning an alkaline solution of pyrogallic acid black.

In the synthetical method, water is decomposed in a eudiometer, as in the analytical method, and the two gases collected together and an electric spark passed through the mixture. Combination of the two gases takes place instantaneously, with the production of water. (A slight quantity of hydrogen may remain uncombined, due to some of the gaseous oxygen evolved in the decomposition of the water remaining in solution in water, thereby leaving the quantity of oxygen in the gaseous mixture slightly inadequate for the hydrogen.)

The synthesis of water may also be performed by passing a slow stream of pure, dry hydrogen over a weighed quantity of hot cupric oxide, CuO, contained in a porcelain boat in a Bohemian glass combustion tube. The hydrogen is best obtained from the action of zinc on sulphuric acid, and purified and dried by passing it through two Woulff's bottles containing respectively solutions of sodium hydroxide and argentic nitrate, and then through a drying tube containing pieces of calcium chloride.

The hydrogen will deprive the hot cupric oxide of its oxygen, reducing it to metallic copper, and vapor of water will be formed. By accurately collecting and weighing the water produced, and also determining the weight of reduced copper, the relative weights of oxygen and hydrogen present in the water obtained may be determined.

The composition of water may also be shown by burning a known weight of hydrogen with cupric oxide, collecting and weighing the resulting water and estimating the oxygen indirectly.

Properties : A colorless, tasteless, odorless liquid.

1 cubic centimetre of pure water at 4° C., and 760 millimetres pressure weighs 1 gramme.

1 litre (1000 c.c.) of pure water at 4° C. and 760 millimetres pressure weighs 1000 grammes.

1 cubic inch of pure water at 62° F. and 30 inches pressure weighs 252.45 grains.

1 cubic inch of pure water in vacuum weighs 252.74 grains.

1 cubic foot measures about 7½ gallons.

Water is at its maximum density at 4° C. or 39.2° F.

Its range of liquidity is from 0° C. to 100° C. or 32° F. to 212° F.

The temperature of water in closed vessels, at perfect rest and out of contact with air, may be lowered to about 14° F. or —10° C. without solidification. If water at this temperature be agitated it instantly freezes, the temperature rising at once to 32° F. or 0° C.

The boiling point of water (100° C.) is increased by its containing solids in solution. The boiling point is also increased when the water is under pressure.

Water evaporates at all temperatures.

The absolute boiling point of water is 370° C. (critical temperature of water), at which point its vapor tension is equivalent to a pressure of 195.5 atmospheres. At the ordinary temperature, and a pressure of 1 atmosphere, it boils at 100° C.

Water under a pressure of 195.5 atmospheres and heated to 370° C. passes into vapor. If heated to 371° C. no amount of pressure will keep it in the liquid state. Water cannot exist in the liquid state at a temperature above 370° C. and under a pressure of 195.5 atmospheres.

Moist air occupies more space than dry air, due to the vapor of water present.

Boiling Point of Water at Different Elevations.

Elevation.	Height of Barometer.	Temperature F°.
0 feet	30.0 inches.	212.0
131 "	29.76 "	211.6
518 "	29.33 "	210.9
755 "	29.06 "	210.4
1558 "	28.19 "	209.1
6240 "	23.58 "	200.0
11870 "	19.02 "	190.2

Chemical relations of water: It is a neutral substance. It is capable of entering into a large range of combinations.

Examples:

$$H_2O + SO_3 = H_2SO_4.$$
$$H_2O + K_2O = 2KOH.$$

Thus, water may enter into combination to form electro-negative as well as electro-positive compounds, *i. e.*, it unites with anhydrides to form acids, and with bases to form hydroxides.

It enters into combination with salts as water of crystallization and as water of constitution (saline water).

Water of crystallization may be expelled from a compound by heating the compound at a temperature of 100° C.

Water of constitution (saline water) cannot be expelled at a temperature of 100° C.

Example:

Magnesium sulphate, $MgSO_4 + 7H_2O$.

Six of the seven molecules of water in magnesium sulphate may be expelled at a temperature of 100° C.; the remaining molecule cannot be expelled except at a higher temperature.

Water of crystallization in a compound is sometimes represented by the abbreviation *aq.;* thus, $MgSO_4 + 7$ aq.

Substances which give off their water of crystallization at ordinary temperature are termed efflorescent,—are said to effloresce.

Substances which absorb water from the air are termed deliquescent,—are said to deliquesce.

Water may be recognized by—

1. Its freedom from taste, odor and color.
2. Its specific gravity (1000).
3. Its boiling at 100° C.
4. Subjecting it to the action of a current of electricity, thereby decomposing it into hydrogen and oxygen.

Solvent properties of water: It has the greatest range of solvency of any known liquid. Owing to its great solvent action, it is never found pure in nature. It is purest in the form of rain water.

When 1 part of a substance is soluble in 100 parts of water at a given temperature, it is said to be soluble, and when 1 part of a substance is insoluble in 100 parts of water, it is said to be insoluble.

1 part of magnesium sulphate is soluble in 1½ parts by weight of water.

1 part of calcium sulphate is soluble in 500 parts by weight of water.

1 part of strontium sulphate is soluble in 10,000 parts by weight of water.

1 part of barium sulphate is soluble in 200,000 parts by weight of water.

When water at ordinary temperature holds as much of a solid in solution as is possible, it is said to be saturated.

Temperature and pressure have an influence on solubility.

Divisions of water: (*a*) Chalybeate water, in which iron is the predominant constituent.

(*b*) Magnesian water, in which magnesium is the predominant constituent.

(*c*) Sulphur water, in which hydrogen sulphide is the predominant constituent.

(*d*) Carbonated water, in which carbon dioxide is the predominant constituent.

Hard and soft waters: Hard water possesses the property of decomposing soap with the production of an insoluble compound.

Soft water does not possess the property of decomposing soap with the production of an insoluble compound, but produces a lather with soap.

Soap is a definite chemical compound—a stearate, oleate, palmitate, etc., of an alkali. Soaps are produced by the action of a free fixed alkali, *i. e.*, caustic potash or caustic soda, on animal or vegetable fats or oils.

If caustic potash be used in the saponification of the fat, the resulting soap is a "soft soap." If caustic soda be used instead of potash, the resulting soap is a "hard soap."

The fats are—

Palmitine.

Margarine.

Stearine.

They are compounds of palmitic, margaric, or stearic acid with glycerin, $C_3H_5(OH)_3$, a triatomic alcohol—*i. e.*, palmitate, margarate and stearate of glyceryl.

Palmitic acid is $C_{16}H_{32}O_2$.
Margaric " " $C_{17}H_{34}O_2$.
Stearic " " $C_{18}H_{36}O_2$.

One atom of hydrogen in stearic acid is replaceable, and, therefore, the acid may be represented, $HC_{18}H_{35}O_2$.

The combination of glycerin with stearic acid may be represented as follows:

$$\underset{\text{Glycerin.}}{C_3H_5(OH)_3} + \underset{\text{Stearic Acid.}}{3HC_{18}H_{35}O_2} = \underset{\text{Glyceryl Stearate.}}{C_3H_5(C_{18}H_{35}O_2)_3} + 3H_2O.$$

When glyceryl stearate is boiled with a solution of caustic soda, a new compound, sodium stearate,—hard soap—is formed. Glycerin is produced at the same time.

$$\overset{\text{Glyceryl Stearate.}}{C_3H_5(C_{18}H_{35}O_2)_3} + 3NaOH = \overset{\text{Sodium Stearate.}}{3NaC_{18}H_{35}O_2} + \overset{\text{Glycerin.}}{C_3H_5(OH)_3}.$$

When soap, for example, sodium stearate, is brought in contact with a hard water, *i. e.*, a water containing soluble salts of calcium, magnesium, etc., decomposition of the soap occurs and new compounds are produced.

In the case of water containing calcium bicarbonate in solution, insoluble calcium stearate is formed, according to the following reaction:

$$\overset{\text{Sodium Stearate.}}{2NaC_{18}H_{35}O_2} + CaCO_3,H_2CO_3 = \overset{\text{Insol. Calcium Stearate.}}{Ca(C_{18}H_{35}O_2)_2} + \overset{\substack{\text{Sodium Acid.}\\ \text{Carbonate.}}}{2NaHCO_3}.$$

The hardness of water, or really its soap-destroying power, is determined by means of a standard solution of soap. The standard soap solution is prepared so that 14.25 c.c. of it shall contain just sufficient soap to combine with the calcium equivalent to 0.010 gramme (10 milligrammes) of calcium carbonate contained in 50 c.c. water and produce a lather in the same. The hardness of water is always represented in units of calcium carbonate.

In order to standardize the soap solution, a solution containing a known quantity of a salt of calcium is prepared by dissolving 0.2 gramme precipitated calcium carbonate in dilute hydrochloric acid, thereby converting it into soluble calcium chloride, evaporating the remaining undecomposed acid and dissolving the residue in distilled water and diluting to a volume of 1000 c.c.

Then

$CaCO_3$.
1000 c.c. = 0.200 gramme.
100 c.c. = 0.020 "
50 c.c. = 0.010 "
10 c.c. = 0.002 "
1 c.c. = 0.0002 "

The standard soap solution is prepared by dissolving about 15 grammes of white castile soap in alcohol of about 56 per

cent. strength, and diluting with alcohol of the same strength to a volume of 1000 c.c.

In standardizing the soap solution, 50 c.c. of the standard solution containing the salt of calcium are placed in a flask of about 200 c.c. capacity. The soap solution is added, a little at a time, from a burette, the mouth of the flask is closed with the thumb or a cork, and vigorously agitated with an up and down movement, after each addition of soap solution, until finally a lather lasting five minutes is produced. Quite likely, as above prepared, the soap solution will be too strong, and, therefore, less than 14.25 c.c. will be required for the 50 c.c. of standardizing solution of calcium salt.

Suppose 11.25 c.c. soap solution had been required. It is then too strong by 3 c.c. *i. e.*, the difference between 11.25 c.c. and 14.25 c.c. Therefore, to every 11.25 c.c. of soap solution remaining there must be added the difference between 11.25 c.c. and 14.25 c.c. or 3 c.c. of 56 per cent. alcohol.

Example:

1000 c.c. soap solution.
11.25 c.c. used.
11.25) 988.75 c.c. remaining.
87.884 × 3 = 263.6 c.c. of 56 per cent. alcohol

to be added to the 988.75 c.c. soap solution, so that exactly 14.25 c.c. of the solution shall be required to produce a lather (lasting five minutes), with 50 c.c. of the solution of calcium salt.

Method: 50 c.c. of the water under examination are placed in a flask, and the standard soap solution added, a little at a time, from a burette, and the flask closed and vigorously agitated with an up and down movement after each addition of soap solution until a lather lasting five minutes is produced. Suppose 4 c.c. of the soap solution were required to produce the lather. By reference to the table (see page 78) it is found that the hardness of that particular water is equivalent to 4.57 parts of $CaCO_3$, in 100,000 parts of water. (Total hardness)

If more than 16 c.c. of the soap solution should be required to produce a lather in 50 c.c. of water, the operation must be repeated upon a smaller volume (25 or 10 c.c.) of water, the volume being made up to 50 c.c. by the addition of distilled water before adding the soap solution. The degrees of hardness must then be multiplied according to the degree of dilution.

Table of Hardness in Parts of Calcium Carbonate per 100,000 Parts of Water, 50 c.c. of Water being Used.

c.c. of Soap Sol.	$CaCO_3$ per 100,000.	c.c. of Soap Sol.	$CaCO_3$ per 100,000.
0.7	0.00	9.0	11.80
1.0	.48	10.0	13.31
2.0	1.95	11.0	14.84
3.0	3.25	12.0	16.43
4.0	4.57	13.0	18.02
5.0	6.00	14.0	19.00
6.0	7.43	14.25	20.00
7.0	8.86	15.0	21.19
8.0	10.30	16.0	22.86

Temporary and permanent hardness of water: Most waters become softer on boiling, owing to the decomposition of the soluble bicarbonates of calcium and magnesium; carbon dioxide being set free, and insoluble calcium carbonate being precipitated.

$$CaCO_3,H_2CO_3 = CO_2 + H_2O + CaCO_3.$$

The hardness which disappears on boiling the water is known as **temporary hardness,** whilst that which remains after boiling is known as **permanent hardness.**

In determining temporary and permanent hardness, 200 c.c. of the water are placed in a flask of about 300 c.c. capacity and boiled briskly for half an hour. When cool, the volume is made up to 200 c.c. with distilled water, and 50 c.c. of the liquid are taken and titrated as above in the determination of the total hardness. The hardness so found is **permanent** hardness, and by subtracting it from the total hardness the **temporary** hardness is obtained.

drying and weighing the residue as above given. The number of milligrammes of residue obtained from 70 c.c. water will correspond to the number of grains per imperial gallon.

70 c.c. water = 70,000 milligrammes (70.0 grammes).
1 gallon " = 70,000 grains.

In water analysis, the volume 70 c.c. is often termed the "miniature gallon," in which the milligramme corresponds to the grain, and, therefore, the number of milligrammes of substance found in a volume of 70 c c. water corresponds to the number of grains per gallon.

QUALITATIVE DETECTION AND QUANTITATIVE ESTIMATION OF INORGANIC CONSTITUENTS.

A large quantity, not less than 1 litre, of the water, to which a few drops of hydrochloric acid have been added, is evaporated to dryness in a platinum dish. The residue is dissolved in a small volume of water, and the analysis carried on according to the methods in ordinary qualitative and quantitative mineral analysis.

Determination of the organic matter in water: 1. **By igniting the weighed residue** from a given quantity of water and determining the loss in weight. This method does not give accurate results, because in the ignition certain of the mineral constituents undergo change; for example, calcium carbonate when heated is converted into calcium oxide, with the evolution of carbon dioxide, thus causing a diminution in the weight of the residue which might be erroneously attributed to loss occasioned by organic matter.

$$CaCO_3 = CaO + CO_2.$$

A blackening of the residue on heating the dish over the naked flame indicates the presence of organic matter.

2. **Frankland's combustion process,** in which the organic elements in water are determined by submitting the residue left on evaporation to combustion with cupric oxide, and measuring the carbon dioxide and nitrogen given off by means of gasometric methods. This is the most satisfactory method for the determination of carbon and nitrogen in organic

combination in water, but the cost of the special apparatus and the delicacy of manipulation required in the performance of the method render it rather unavailable for the physician.

3. **Forchhammer or oxygen process**: This method depends upon the varying amounts of oxygen absorbed from a solution of potassium permanganate by the same volumes of waters of different organic purity, or, the quantity of oxygen required to oxidize the organic matter in a given volume of water in a given time.

Potassium permanganate, $K_2Mn_2O_8$, is the substance used to furnish the oxygen, *i. e.*, the oxidizing agent. In the presence of sulphuric acid potassium permanganate yields oxygen to organic matter.

Reactions occurring in the method:

(*a*) $\overset{316}{K_2Mn_2O_8} + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + \overset{80}{O_5}$.

(One molecule of $K_2Mn_2O_8$ in the presence of H_2SO_4 and organic matter yields five atoms of oxygen.)

$$(b)\ K_2Mn_2O_8 + 10KI + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 8H_2O + I_{10}.$$

(One molecule of $K_2Mn_2O_8$ and ten molecules of potassium iodide, KI, undergo mutual decomposition with the liberation of ten atoms of iodine.)

$$(c)\ 2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

(Two molecules of sodium thiosulphite, $Na_2S_2O_3$, with two atoms of iodine form sodium iodide, NaI, and sodium tetrathionate, $Na_2S_4O_6$.)

Preparation of the solutions: 1. Potassium permanganate solution.

Once the molecular weight of $K_2Mn_2O_8$ (316), expressed in milligrammes, is dissolved in 1000 c.c. distilled water.

Then,

		Potass. Permanganate.		Oxygen.
1000 c.c.	=	0.316	=	0.080.
100 c.c.	=	0.0316	=	0.008.
10 c.c.	=	0.00316	=	0.0008.
1 c.c.	=	0.000316	=	0.00008.

2. Sodium thiosulphite ($Na_2S_2O_3 + 5H_2O$) solution.

One molecule of $K_2Mn_2O_8$ acting upon KI, sets free ten atoms of iodine, and two atoms (one molecule) of iodine require two molecules of $Na_2S_2O_3$; therefore one molecule of $K_2Mn_2O_8$ is equivalent to ten molecules of $Na_2S_2O_3$.

Instead of dissolving one molecule of $Na_2S_2O_3 + 5H_2O = 248$, expressed in milligrammes, in 1000 c.c. water (which would make the $Na_2S_2O_3$ solution too weak for accurate work), four times the molecular weight of $Na_2S_2O_3$, expressed in milligrammes ($4 \times 0.248 = 0.992$), is dissolved in 1000 c.c. distilled water.

1 c.c. of the standard $K_2Mn_2O_8$ solution will then require 2.5 c.c. of the $Na_2S_2O_3$ solution, or 10 c.c. of the $K_2Mn_2O_8$ solution will require 25 c.c. of the $Na_2S_2O_3$ solution.

0.992 gramme $Na_2S_2O_3 + 5H_2O$ are dissolved in 1000 c.c. distilled water.

3. Dilute sulphuric acid.

One part of strong sulphuric acid diluted with three parts of distilled water.

4. Potassium iodide solution.

Ten grammes of potassium iodide are dissolved in 100 c.c. distilled water.

5. Starch solution.

One part of starch rubbed up with twenty parts of boiling-hot water, filtered, and the filtrate boiled and allowed to stand several hours. The clear supernatant liquid is decanted and preserved for use.

Method: 250 c.c. of pure distilled water are placed in each of two flasks of about 500 c.c. capacity. 250 c.c. of the water under examination are placed in each of two other flasks of about 500 c.c. capacity. 10 c.c. of dilute sulphuric acid and 10 c.c. of potassium permanganate solution are placed in each of the four flasks.

After the lapse of one hour, two drops of KI solution are placed in one of the flasks containing the distilled water, and also in one of the flasks containing the water under examination. The purple color of the liquid due to the permanganate is destroyed on the addition of the potassium iodide, leaving a brown color, due to free iodine, in its stead. By this procedure

an amount of iodine will be liberated exactly equivalent to the quantity of undecomposed potassium permanganate present in the water.

Sodium thiosulphite solution is now added to the liquid in each of the two flasks, until the brown color is nearly destroyed, and is then followed by the addition of one drop of starch solution, (a blue color will be produced, due to the action of the free iodine on the starch). The addition of the thiosulphite solution is continued until the blue color is just destroyed. The aggregate number of cubic centimetres of thiosulphite solution required in the operation is noted.

Suppose 25 c.c. of thiosulphite solution were required for the iodine set free by the permanganate in the **distilled water.** 10 c.c. of permanganate solution were added to the 250 c.c. distilled water, and the permanganate in the 10 c.c. is equivalent to 0.0008 gramme oxygen. Therefore, as 25 c.c. thiosulphite solution are equivalent to 0.0008 gramme oxygen, 1 c.c. thiosulphite solution is equivalent to $0.0008 \div 25 = 0.000032$ gramme oxygen.

Suppose 20 c.c. of thiosulphite solution were required for the free iodine in the 250 c.c. **water under examination.** 25 c.c. of thiosulphite solution were required for the control test with distilled water. 5 c.c. less thiosulphite solution were required for the water under examination than in the control test with distilled water, hence some of the permanganate must have been decomposed by the organic matter in the water. As the value of 1 c.c. of thiosulphite solution expressed in oxygen units in this particular experiment is 0.000032 gramme, $5 \times 0.000032 = 0.00016$ gramme oxygen was consumed in one hour by the organic matter in the 250 c.c. water, or—

$4 \times 0.00016 = 0.00064$ grm. oxygen by 1000 c.c. water.
$1000 \times 0.00064 = 0.64$ " " 1,000,000 "

After the lapse of three hours the liquids in the remaining two flasks—containing respectively the distilled water for the control test and the water under examination—are treated exactly as above described.

In reporting the result of the examination, the amount of oxygen consumed in one hour and also the amount of oxygen consumed in three hours by the water under examination, are reported.

A water requiring over 0.25 part of oxygen (equivalent to 1 part potassium permanganate), to oxidize the organic matter contained in 100,000 parts of the water, is considered unfit for domestic purposes.

The presence of reducing substances, such as nitrites, ferrous salts, hydrogen sulphide, etc., interferes with the permanganate or oxygen process for organic matter in water.

The permanganate or oxygen process does not tell the nature of the organic matter, and as the quantity of permanganate reduced by different kinds of organic matter is very variable, it therefore follows that only when the organic matter is of the same kind can comparable results be obtained by this method.

Wanklyn's ammonia process: In this process the nitrogenous organic matter in water is measured by the quantity of ammonia yielded by the destruction of the organic matter.

The ammonia is determined by the intensity of coloration produced with Nessler's reagent, by which 1 part of ammonia in 100,000,000 parts of water can be recognized.

The determination of ammonia in water is of great importance, as the presence of this compound in any but very minute quantity is generally indicative of recent pollution with animal organic matters. The amount of ammonia in sewage usually varies from 2 to 10 parts per 100,000, and in waters polluted by sewage between even still wider limits. In shallow well water it varies from 0 to 2.75 parts per 100,000 parts of water. The presence of ammonia in deep well water is less suspicious, as it is there often derived from the reduction of nitrates.

The ammonia, in solution as such or in combination, which has resulted from the decomposition of nitrogenous organic matter in the water is termed **free ammonia.** The ammonia resulting from the destruction of the nitrogenous organic matter by treatment with certain reagents is termed **albuminoid ammonia.**

Reagents: 1. Nessler's Reagent.

50 grammes potassium iodide (KI) are dissolved in 100 c.c. of distilled water and a saturated solution of mercuric chloride ($HgCl_2$) is added to it until a slight permanent precipitate is formed. (50 grammes KI will require about 22 grammes $HgCl_2$.) 100 grammes of sodium hydroxide, NaOH, or of KOH, are dissolved in 100 c.c. of distilled water and added to the potassium iodide and mercuric chloride solution, and the whole diluted with distilled water to 1000 c.c. After subsidence, the clear yellowish liquid is decanted off and kept in a stoppered bottle ready for use.

On adding the mercuric chloride solution to the potassium iodide solution the following reaction occurs:

$$4KI + HgCl_2 = 2KCl + (KI)_2HgI_2.$$

The action of the ammonia (NH_3) on Nessler's solution may be represented—

$$\overset{\text{Molec. Wt. 17.}}{NH_3} + 2(KI)_2HgI_2 + 3KOH =$$

$$\overset{\text{Molec. Wt. 559.}}{NHg_2I,H_2O} + 7KI + 2H_2O.$$

17 parts of NH_3 produce 559 parts of NHg_2I,H_2O.

2. Water free from ammonia.

Distilled water, or ordinarily good water, is treated with potassium hydroxide, KOH, or sodium hydroxide, NaOH, and potassium permanganate, $K_2Mn_2O_8$, and allowed to stand 24 hours. It is then distilled, and small portions of the distillate are collected at intervals and tested with Nessler's reagent. The distillate is rejected as long as it produces a coloration with Nessler's reagent. The distillate, free from ammonia, is collected in bottles and kept ready for use. The distillation must not be pushed too far, otherwise the final portions of the distillate may contain ammonia resulting from the decomposition of organic substances in the retort.

3. Standard solution of ammonium chloride, NH_4Cl.

Molecular weight of $NH_4Cl = 53 5.$
" " " $NH_3 = 17.$

Every 53.5 parts of NH_4Cl correspond to 17 parts by weight of NH_3.

To determine the quantity of ammonium chloride necessary to prepare 1000 c.c. of solution so that 1 c.c. of it shall contain a quantity of ammonium chloride, NH_4Cl, corresponding to 0.00001 gramme ammonia, NH_3, the following proportion is employed:

$$\overset{NH_3.}{17} : \overset{NH_4Cl.}{53.5} :: \overset{NH_3.}{0.010} : \overset{NH_4Cl.}{0.0315} \text{ grm. containing } 0.010 \text{ grm. } NH_3.$$

0.0315 gramme ammonium chloride is dissolved in 1000 c.c. of water free from ammonia.

Then—

$$\begin{array}{rll} & NH_4Cl. & NH_3. \\ 1000 \text{ c.c.} = & 0.0315 & = 0.010 \\ 100 \text{ c.c.} = & 0.00315 & = 0.001 \\ 10 \text{ c.c.} = & 0.000315 & = 0.0001 \\ 1 \text{ c.c.} = & 0.0000315 & = 0.00001 \end{array}$$

4. Solution of potassium permanganate and potassium hydroxide to decompose nitrogenous organic matter and set "albuminoid ammonia" free.

8 grammes of potassium permanganate and 200 grammes of solid potassium hydroxide are dissolved in 1000 c.c. of distilled water. The solution is boiled in a retort for some time, in order to get rid of all traces of ammonia and nitrogenous organic matter. The distillate is tested at intervals with Nessler's reagent until, finally, a portion of the distillate is found to be free from ammonia. When cool, the solution in the retort is diluted to 1000 c.c., by the addition of water free from ammonia, and placed in well-stoppered bottles.

5. A saturated solution of sodium carbonate, Na_2CO_3.

Dry sodium carbonate is heated for one hour in a platinum dish, without fusing, thereby driving off any ammonia that may have been contained in the carbonate. An excess of the carbonate treated as above is boiled with distilled water and the solution preserved in bottles.

Method: 500 c.c. of the water under examination are placed in a clean retort of about 1½ litres capacity, to which a Liebig's condenser is attached. 10 c.c. of the saturated sodium carbonate solution are added, and the distillation is proceeded

with, the retort being heated with the free flame of a Bunsen burner. The distillation should be slow. The distillate is collected in colorless glass cylinders of about 75 c.c. capacity. Distillation is continued until 50 c.c. of distillate have been collected in each of 3 cylinders,—150 c.c. in the aggregate. The whole of the free ammonia, unless an excessive amount be present, is contained in the first three cylinders of distillate. The three cylinders are covered with watch-glasses and stood aside.

The distillation is stopped a moment, and 50 c.c. of the solution containing potassium permanganate and potassium hydroxide are added to the 350 c.c. of water remaining in the retort, and the distillation is continued. The distillate which now comes over contains the ammonia, termed "albuminoid ammonia," derived from the decomposition of the nitrogenous organic matter in the water, and is collected in glass cylinders of about 75 c.c. capacity. Distillation is continued, and the distillate collected in 50 c.c. portions until a final portion is obtained which fails to respond to Nessler's test. (1 c.c. of Nessler's reagent is employed in testing.) The cylinders containing the distillate are covered with watch-glasses and stood aside.

On the addition of Nessler's reagent to a solution containing ammonia, a color ranging from yellow to brown is produced, varying in intensity with the quantity of ammonia present.

The free and the albuminoid ammonia, obtained from the water, are determined by comparing the intensity of color produced on the addition of 1 c.c. Nessler's reagent to each cylinder containing 50 c.c. of distillate, and that produced by 1 c.c. Nessler's reagent placed in 50 c.c. of water in which there is a known volume of standard ammonium chloride solution containing a definite quantity of ammonia.

Different volumes of standard ammonium chloride solution, containing definite quantities of ammonia, are placed in each of a series of 6 or 8 colorless glass cylinders, and diluted, in each case, with water free from ammonia, to a volume of 50 c.c. To each cylinder 1 c.c. of Nessler's reagent is added.

Example:

Standard
Cylinder.

No. 0 containing 50 c.c. water free from ammonia + 1 c.c. of Nessler's reagent for comparison.

One c.c. of Nessler's reagent is added to each of the following cylinders:

No. 1 containing 1 c.c. standard NH_4Cl sol. = 0.00001 grm. NH_3.
No. 2 " 2 " " " " = 0.00002 " "
No. 3 " 3 " " " " = 0.00003 " "
No. 4 " 5 " " " " = 0.00005 " "
No. 5 " 7 " " " " = 0.00007 " "
No. 6 " 9 " " " " = 0.00009 " "

Example: 1 c.c. of Nessler's reagent is added to the distillate containing the free ammonia in each of the first series of three cylinders. The color produced is compared with the shades of color in the cylinders holding standard ammonium chloride solution, containing a known quantity of ammonia.

Suppose the intensity of color produced in the first of the three cylinders corresponds with the color in cylinder No. 5 of the standard ammonia solution, the second cylinder with No. 3 of the standard solution and the third with No. 1 of the standard solution. Then, of free ammonia there is present—

1st cylinder (corresponds with No. 5, standard above) = 0.00007 grm. NH_3.
2d " " " " 3, " " = 0.00003 " "
3d " " " " 1, " " = 0.00001 " "
Total free ammonia in 500 c.c. of the water = 0.00011 grm.

0.00011 × 2 = 0.00022 part per 1000 parts water.
0.00022 × 1000 = 0.22 " " 1,000,000 " "

In a similar manner 1 c.c. of Nessler's reagent is added to the distillate containing the albuminoid ammonia in each of the second series of cylinders.

Suppose the intensities of color produced in the cylinders correspond as follows:

1st cylinder (corresponds with No. 6, standard, page 88) = 0.00009 grm. NH_3.
2d " " " " 4, " " = 0.00005 " "
3d " " " " 1, " " = 0.00001 " "
Total albuminoid ammonia in ———
500 c.c. of the water = 0.00015 grm.

0.00015 × 2 = 0.0003 part per 1000 parts water.
0.0003 × 1000 = 0.3 " " 1,000,000 " "

Water yielding from 0.00 to 0.05 part albuminoid ammonia per 1,000,000 parts of water is classed as a very pure water. Water yielding from 0.05 to 0.10 part albuminoid ammonia per million parts of water is classed as somewhat doubtful. When it yields 0.10 to 0.15 part per million it is classed as very suspicious; and when it yields over 0.15 part per million of albuminoid ammonia it is classed as absolutely unfit for domestic use.

Determination of the Total Nitrogen of the Organic Matter in Water by Converting it into Ammonia by Kjeldahl's Method.

Method: 500 c.c. of the water are placed in a flask, which is then attached to a Liebig's condenser and heated until 200 c.c. have distilled over. In this volume of 200 c.c. the quantity of free ammonia is determined by Nesslerizing, as in Wanklyn's process. The water remaining in the flask is cooled, and 10 c.c. of concentrated sulphuric acid are added and thoroughly mixed by agitating the flask. The flask is now inclined and the liquid boiled until it has a syrupy appearance and the water has been wholly expelled. The latter point is determined by the liquid in the flask becoming pale yellow in color or colorless. The flask is removed from the flame and powdered potassium permanganate is added, in small portions at a time, until the liquid becomes green in color (if purple, the water was not completely expelled). The liquid is now cooled, and 200 c.c. of water, free from ammonia, and 100 c.c. of sodium hydroxide solution (strength 1–5) are added, and the flask is again connected with a Liebig's condenser. The liquid is distilled, slowly at first, into dilute hydrochloric acid, until about 50 c.c. are distilled, and then the delivery tube is rinsed, and distillation is continued until 150 or 175 c.c. inclusive of the first-mentioned 50 c.c., have distilled over. The aggregate volume distilled is diluted with water, free from ammonia, to a volume of 250 c.c., and from this 50 c.c. are taken and Nesslerized after the manner described in **Wanklyn's ammonia process** (page 88).

The sodium hydroxide solution used in the above method is prepared by dissolving 200 grammes of sodium hydroxide and 2 grammes of potassium permanganate in 1250 c.c. of distilled water, and boiling until the volume is reduced to 1000 c.c. or less. (If less, it is to be diluted with water, free from ammonia, to 1000 c.c.)

Quantitative Determination of Nitrites in Water.

Griess' Method depends upon the production of an intense rose-red color, due to the formation of azobenzolnaphthylamine sulphonic acid, on the addition of sulphanilic acid followed by naphthylamine hydrochloride to an acidified solution of a nitrite.

By this method 1 part of nitrous acid may be detected in 100,000,000 parts of water (100 c.c. of the water being used).

Reagents required: 1. Sulphanilic acid, 1 part of the acid dissolved in 100 parts of water.

2. Naphthylamine hydrochloride, 1 part of the salt dissolved in 100 parts of water.

3. A solution of potassium nitrite, KNO_2, so that 1 c.c. shall contain 0.00001 gramme nitrous oxide, N_2O_3.

4. Dilute sulphuric acid, 1 part of sulphuric acid with 2 parts of water.

Preparation of the standard solution of potassium nitrite, KNO_2: Argentic nitrite, a compound easily weighed, is selected for this purpose. The required quantity of argentic nitrite is weighed off, dissolved in water, and treated with a quantity of potassium chloride adequate to completely precipitate the silver of the argentic nitrite in the solution. Double

decomposition occurs, the silver is precipitated and the nitrous acid remains in solution in combination with potassium as potassium nitrite.

To determine the quantity of argentic nitrite necessary to prepare 1000 c.c. of standard solution so that each cubic centimetre shall contain 0.00001 gramme N_2O_3, the following proportion is employed:

$$\overset{N_2O_3.}{76} : \overset{AgNO_2.}{308} :: \overset{N_2O_3.}{0.010} : \overset{AgNO_2.}{0.0405} \text{ gramme}$$

0.0405 gramme of argentic nitrite is dissolved in hot water, potassium chloride added, in slight excess, to precipitate the silver, and the whole diluted to 1000 c.c. When the argentic chloride has subsided, the supernatant clear liquid is decanted and preserved for use.

$$\begin{array}{lcl} & & N_2O_3. \\ 1000 \text{ c.c. of the solution} & = & 0.01 \\ 100 \text{ c.c. `` ``} & = & 0.001 \\ 10 \text{ c.c. `` ``} & = & 0.0001 \\ 1 \text{ c.c. `` ``} & = & 0.00001 \end{array}$$

Method: 100 c.c. of the water under examination are placed in a colorless glass cylinder, and a few drops of dilute sulphuric acid are added, followed by the addition of 2 c.c. of sulphanilic acid and 2 c.c. of naphthylamine hydrochloride solutions.

Immediately after the above operation, different volumes (0.3 to 2.5 c.c.) of standard nitrite solution are placed in several colorless glass cylinders, each cylinder filled to 100 c.c. with distilled water, and to each consecutively are added a few drops of dilute sulphuric acid, 2 c.c. sulphanilic acid and 2 c.c. of naphthylamine hydrochloride solutions.

On standing twenty minutes, the intensity of rose-red color produced in the water under examination is compared with the color produced in the distilled water containing known quantities of nitrite. The quantity of nitrite is calculated in a manner similar to that employed in determining the quantity of ammonia with Nessler's reagent (page 88).

According to the recent observations of Ilosway, the reagents in **Griess' Method** may be prepared as follows:

1. Dissolve 0.5 gramme of sulphanilic acid in 150 c.c. dilute acetic acid.

2. Boil 0.1 gramme of naphthylamine hydrochloride in 20 c.c. water; decant the colorless liquid and add 150 c.c. of dilute acetic acid.

Application: To 50 c.c. of the water under examination, add about 2 c.c. of sulphanilic acid solution, then about an equal volume of naphthylamine hydrochloride solution. If the water contains N_2O_3, even in the proportion of 1 in 1,000,000,000 parts of water, the mixture will acquire a red coloration in about one minute.

The reaction is equally delicate if the reagents be mixed before being added to the water.

HYDROGEN PEROXIDE. H_2O_2.

Molecular weight, 34. Density in liquid state, 1.45.

History: Discovered by Thenard in 1818 and investigated by Brodie and by Schoenbein in 1850.

Preparation: Barium peroxide, BaO_2, is mixed with water and then treated with dilute hydrochloric acid, sulphuric acid, or phosphoric acid.

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$
$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$
$$BaO_2 + H_3PO_4 = BaHPO_4 + H_2O_2.$$

The hydrogen peroxide is obtained from the mixture by agitating it with ethyl ether, allowing the latter to separate as a layer above the water, then decanting and allowing the ether to evaporate at ordinary temperature. Hydrogen peroxide, which was dissolved by the ether, will remain in the vessel.

Properties: (*a*) Physical. A colorless and, when concentrated, syrupy liquid, having a slight odor resembling that of a dilute solution of chlorine.

It has a bleaching action on the skin, and in concentrated form has corrosive action, with the production of a painful sore.

When heated it undergoes decomposition.

(*b*) Chemical. In contact with ozone decomposition occurs, water is produced and oxygen is set free.

$$H_2O_2 + O_3 = H_2O + 2O_2.$$

It is a powerful oxidizing agent, converting certain lower oxides of the elements into higher oxides.

$$As_2O_3 + H_2O_2 = As_2O_5 + H_2.$$

It also acts as a reducing agent, reducing certain oxides of the metals to the metallic state.

$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2.$$

Tests: 1. It liberates iodine from potassium iodide.

$$2KI + H_2O_2 = 2KOH + I_2.$$

Ozone acts similarly upon potassium iodide.

$$O_3 + 2KI + H_2O = 2KOH + O_2 + I_2.$$

2. Ozone tarnishes a bright surface of metallic silver; hydrogen peroxide does not.

3. Hydrogen peroxide reduces chromic acid, H_2CrO_4, to perchromic acid $H_2Cr_2O_8$.

$$H_2O_2 + 2H_2CrO_4 = 2H_2O + H_2Cr_2O_8.$$

The perchromic acid imparts a blue color to the liquid.

It reduces permanganic acid, or permanganates.

$$\underset{\text{Potass. Permanganate.}}{K_2Mn_2O_8} + H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 4H_2O + 3O_2.$$

This action is taken advantage of in the quantitative determination of H_2O_2.

Uses of H_2O_2: It has been employed in medicine externally as a lotion and internally in cases of diabetes mellitus and oxaluria. Lately it has come into favor as a disinfecting agent in cleansing abscess cavities, etc.

It is the chief constituent of the liquids used for bleaching hair, such as "Golden Hair Dye," etc.

Hydrogen peroxide is employed in the detection of blood stains. When H_2O_2 is added to an alcoholic solution of guaiacum containing blood-coloring matter, a beautiful blue coloration is produced.

Practical application of the test: The suspected blood stain is moistened with an alcoholic solution of guaiacum, and then with a few drops of an ethereal solution of hydrogen peroxide. If blood-coloring matter be present, a blue color will be **promptly** produced. It must be remembered that substances other than blood-coloring matter, under the same conditions, will yield a blue color; but the coloring matter of the blood is the only **red** substance known that, under these conditions, will **promptly** yield a blue color.

This test serves simply to indicate that the coloring matter of blood is present, and does not enable us to distinguish the blood of one animal from that of another.

The only method yet known for discriminating between the blood of different animals is by means of the microscope in determining the **form** and **size** of the blood corpuscles. But even this instrument does not enable us to determine positively from which particular animal the blood was derived; thus, several animals have blood corpuscles not only of like form but practically of the same size as those found in man, viz., $\frac{1}{3250}$ of an inch in diameter.

NITROGEN. N.

Atomic weight, 14. Molecular weight, 28. Equivalent weight, 14. Valence I, III, V.

14 grammes of nitrogen measure 11.16 litres. 1 litre weighs 1.256 gramme. Specific gravity compared with air, 0.971.

History: In 1772 Rutherford, impressed by the change produced in atmospheric air by respiration, suggested that it was composed of two gases, and not an element, and that in the act of breathing, one of these gases was abstracted. The gas remaining was called by Rutherford **mephitic air.** Priestley called it **phlogisticated air.** Scheele and Lavoisier, in 1777, independently, proved that air was a mixture of the newly discovered oxygen with another gas, which Lavoisier called **azote.** Cavendish, in 1789, recognized it as one of the constituents of nitre, and, therefore, named it **nitrogen.**

Natural history: It is found in the free state in air (about $\frac{4}{5}$ of air is nitrogen) and in gaseous emanations from volcanoes

It is found in combination in nitrates and in ammonia. It is present in small quantities, in combination, in most products of plant life—as in albumin, alkaloids, etc. In the animal kingdom it is found in combination in all fluids and tissues. It is one of the products (in the form of ammonia) of the decomposition of many nitrogenous organic substances.

In itself it is an inert substance, but some of its combinations with other elements are most virulent poisons, as cyanogen, CN, and the alkaloids, strychnine, brucine, etc.

Preparation: 1. By burning phosphorus in air thereby abstracting oxygen from the air. The phosphorus combines with the oxygen to form phosphoric anhydride, P_2O_5, leaving nitrogen free.

2. By passing chlorine through a solution containing an excess of ammoniacal gas.

$$4NH_3 + 3Cl = 3NH_4Cl + N.$$

In this method care must be exercised that an excess of chlorine is not passed through the solution, because of its liability to form nitrogen trichloride, NCl_3, a highly explosive compound.

3. By heating ammonium nitrate with finely divided metallic zinc.

$$NH_4NO_3 + Zn = ZnO + 2H_2O + N_2.$$

4. By heating a mixture of ammonium chloride and potassium nitrite.

$$NH_4Cl + KNO_2 = KCl + 2H_2O + N_2.$$

5. By heating ammonium nitrite.

$$NH_4NO_2 = 2H_2O + N_2.$$

6. By slowly passing a current of air over red-hot metallic copper.

$$N + O + Cu = CuO + N.$$

In this method, if the air be mixed with ammoniacal gas, the process will become a continuous one, thus—

$$2NH_3 + 3CuO = 3H_2O + Cu_3 + N_2.$$

Physical properties: A colorless, tasteless, odorless gas, neither combustible nor a supporter of combustion. Very slightly soluble in water. Water dissolves about 2 per cent. by volume, of nitrogen.

Its critical temperature is about —146° C., and its critical pressure is about 33 atmospheres. Under these conditions it becomes liquid.

Physiological properties: It is not poisonous in itself—we breathe it daily with oxygen as air—but an animal placed in an atmosphere composed wholly of nitrogen dies because of the absence of oxygen. In air it serves as a diluent of oxygen.

Chemical properties: It is an extremely inert substance, combining directly with only a few elements. A mixture of nitrogen and hydrogen will remain uncombined, but when these gases are in the nascent state they enter into combination to form ammonia, NH_3.

Special characteristics: It is recognized chiefly by its negative properties. It is neither combustible nor a supporter of combustion.

Its presence in an organic substance may be determined, provided it is not present as an oxide, by heating the substance with a fixed alkali—soda-lime. The nitrogen will be evolved in combination as ammonia, NH_3, which latter may be detected by its odor, etc. If in combination as an oxide it may be detected by heating the organic substance with metallic sodium. A cyanide of sodium will be formed, which may be detected by the usual tests for a cyanide.

Nitrogen in combination as ammonium may be detected by warming the compound with sodium hydroxide. Ammoniacal gas will be evolved.

ATMOSPHERIC AIR.

Special history: The ancient alchemists considered air to be one of the four elements. In 1772 Rutherford discovered nitrogen, in 1774 Priestley discovered oxygen, and in 1777 Lavoisier proved that air consisted of these two gases—nitrogen and oxygen.

The nitrogen and oxygen in air are not in chemical combination, but simply mixed mechanically.

Determination of the composition of air: 1. By slowly passing a known volume of air over a weighed quantity of red-hot metallic copper, the oxygen will be retained by the copper forming cupric oxide, and nitrogen will pass uncombined. The increase in the weight of the copper after the operation will indicate the quantity of oxygen taken up, and the uncombined gas collected in a eudiometer will indicate the quantity of nitrogen in the given volume of air.

2. By the slow absorption of oxygen by phosphorus. A eudiometer containing a known volume of air is inverted over water and a piece of phosphorus placed in it. Slow oxidation of the phosphorus takes place with the absorption of oxygen to form phosphoric anhydride, which, with the water present, remains in solution as phosphoric acid. The nitrogen remains unabsorbed. Diminution of volume of the original air occurs, and for every 21 volumes of oxygen absorbed 79 volumes of nitrogen remain.

3. By means of an alkaline solution of pyrogallic acid. The oxygen of the air will be absorbed by the solution, the nitrogen remaining unabsorbed.

4. By exploding air with hydrogen in a eudiometer.

Example: Suppose 100 volumes of air are placed in a eudiometer and 50 volumes of hydrogen added to it. The total volume of gas in the eudiometer is now 150 volumes. On passing an electric spark, through the mixture, the oxygen combines with a sufficient quantity of hydrogen to form vapor of water, which is condensed, thus causing a diminution of the original volume. The 150 volumes diminish to 87 volumes.

$$150 - 87 = 63 \text{ volumes lost.}$$

Of the 63 volumes lost, due to condensed vapor of water, one-third is oxygen, hence $63 \div 3 = 21$ volumes of oxygen in 100 volumes of air.

Oxygen and nitrogen are the chief constituents of air. They are present in the proportion:

	By Volume.		By Weight.	
Oxygen, . .	20.898 per cent.	(approx. 21.0)	23.01 per cent.	(approx. 23.0)
Nitrogen, .	79.102 "	(" 79.0)	76.99 "	(" 77.0)
	100.000	100.0	100.00	100.0

Percentage of Oxygen and Nitrogen in the Air According to the Analyses of Different Investigators.

	OXYGEN.	NITROGEN.
Dumas,	20.81	79.19
Regnault,	20.96	79.04
Liebig.	20.89	79.11
Bunsen,	20.92	79.08
Deville,	20.88	79.12
Wurtz,	20.93	79.07
Average,	20.898	79.102

In addition to oxygen and nitrogen, other substances are present in small quantities in the air, namely—

Aqueous vapor: The quantity of aqueous vapor present varies considerably with the temperature of the air.

Carbon dioxide, resulting from combustion, respiration, and from gases of volcanic origin, etc. It is present in the proportion of from 2 to 4 parts per 10,000 parts of air (0.02 to 0.04 per cent.). Plants take up the carbon of carbon dioxide, setting the oxygen free, thereby preventing an accumulation of the gas in the air. Carbon dioxide may be detected by passing the air or gas containing it through a solution of barium hydroxide or calcium hydroxide. The production of a turbidity, due to the formation of barium or calcium carbonate, indicates the presence of the gas.

Ammoniacal gas, NH_3: Arising from the decomposition of nitrogenous organic substances.

Hydrogen sulphide, H_2S: This gas can hardly be considered a normal constituent of air. It is present in the air of certain localities, *i. e.*, in the neighborhood of volcanoes and in the air of cities. It occurs in the air of cities as the result of the burning of coal of which sulphur is a constituent. It is also derived from springs of sulphuretted water.

Sulphurous anhydride, SO_2, **and sulphuric acid,** H_2SO_4, are always present in the atmosphere surrounding towns, and are derived from the sulphur oxidized in the burning of coal.

Only three oxides of nitrogen combine with the elements of water to form acids, namely:

Hyponitrous Oxide. Hyponitrous Acid.

$$N_2O + H_2O = 2HNO.$$

Nitrous Oxide. Nitrous Acid.

$$N_2O_3 + H_2O = 2HNO_2.$$

Nitric Oxide. Nitric Acid.

$$N_2O_5 + H_2O = 2HNO_3.$$

NITRIC OXIDE OR ANHYDRIDE, N_2O_5. N_2O_5

Molecular weight, 108.

It is the most important of the oxides of nitrogen.

Special history: It was recognized by Geber in the seventh century. In 1785 Cavendish determined that, in combination as nitric acid, it was composed of nitrogen and oxygen. Gay-Lussac and Davy determined the proportions in which the nitrogen and oxygen were present, and in 1849 Deville isolated the compound.

Natural history: It is never found in the free state in nature, but always in combination as native nitrates, almost entirely as potassium nitrate, KNO_3 (saltpetre), or sodium nitrate, $NaNO_3$ (Chili saltpetre). It is found in small quantity in the atmosphere in combination as nitric acid, or as ammonium nitrate. It is also, in combination as a nitrate, a constituent of many vegetable juices.

Preparation: It is formed when a discharge of electricity occurs in the atmosphere, and is also one of the products of the decomposition of vegetable and animal nitrogenous organic substances.

The method usually employed for its preparation is to pass dry chlorine over hot argentic nitrate, $AgNO_3$.

$$2AgNO_3 + Cl_2 = 2AgCl + N_2O_5 + O.$$

Properties: Below a temperature of 30° C. it is a colorless, crystalline solid. It melts at 30° C. and boils at 45° C. Its specific gravity in the solid state is 1.64, and in the liquid state 1.63.

It has an intense affinity for water, combining with it to form nitric acid, the combination being attended with great increase of temperature. One molecule of N_2O_5 unites with one molecule of H_2O to form two molecules of nitric acid.

NITRIC ACID, HNO_3. (AQUA FORTIS.)

Molecular weight, 63.

Preparation: By heating a native nitrate, as potassium or sodium nitrate, in a retort with sulphuric acid.

1. $KNO_3 + H_2SO_4 = \overset{\text{Acid Potassium Sulphate.}}{KHSO_4} + HNO_3.$
2. $2KNO_3 + H_2SO_4 = \overset{\text{Neutral Potassium Sulphate.}}{K_2SO_4} + 2HNO_3.$
3. $2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$

Nitric acid distills over and is collected in a receiver. Some of the lower oxides of nitrogen usually collect with the nitric acid in the receiver, and are removed by passing a stream of pure, dry air through the acid.

In preparing the acid commercially, the molecular proportions (one molecule of KNO_3 and one molecule of H_2SO_4), as given in the first reaction, are preferred to the second, because, owing to its greater solubility, the acid potassium sulphate produced in the reaction is more easily removed from the retort than neutral potassium sulphate.

Sodium nitrate is preferred in the commercial preparation of the acid, because it yields a greater amount of the acid.

Contaminations: Nitric acid may be contaminated with sulphuric acid which may have been carried over mechanically from the retort. To test for it, the nitric acid is considerably diluted with water, and a solution of barium chloride added. A white cloudiness, or a white precipitate, indicates the presence of sulphuric acid.

The acid may contain chlorine in combination as hydrochloric acid. To test for it, the nitric acid is diluted with water, and argentic nitrate solution added. A white cloudiness, or a curd-like precipitate, indicates the presence of chlorine. It may contain iron, which may be tested for by diluting the acid with water, partly neutralizing with pure sodium or potassium carbonate, and testing with potassium sulphocyanide. A ruby-red color indicates the presence of iron.

Nitric acid may contain arsenic, derived from the sulphuric acid employed in its preparation. The acid may be tested for arsenic by diluting it with water, neutralizing with sodium carbonate and applying Marsh's test.

Properties: Nitric acid is a liquid which, in its most concentrated form (mono-hydrate), has a specific gravity of 1.517. The acid of this specific gravity boils at a temperature of 84° C. This, however, is not its true boiling point, the ebullition being due to the decomposition of N_2O_5.

The ordinary nitric acid found in commerce is the trihydrate $(H_2O)_3N_2O_5$, having a specific gravity of 1.42.

Fuming nitric acid is concentrated nitric acid containing lower oxides of nitrogen, as N_2O_3 and N_2O_4.

The ordinary nitric acid, HNO_3, specific gravity 1.42, when pure, is a colorless liquid. The acid, when exposed to sunlight, becomes more or less yellow in color, and sometimes green or blue, due to the presence of oxides of nitrogen, resulting from the decomposition of a small portion of the acid. These oxides may be removed, and the acid rendered colorless, by passing a stream of air through the liquid.

It acts as a powerful oxidizing agent, owing to the large amount of oxygen it contains, which it readily parts with in oxidation. By its action iodine, sulphur, etc., are converted into their highest oxy-acids, whilst lower oxides, as sulphurous, arsenious and phosphorous oxides, are converted into higher oxides. Hot nitric acid oxidizes sulphur, with the formation of sulphuric acid.

It decomposes organic bodies and stains substances of albuminous nature yellow. It decomposes the skin, with the production of picric acid, which latter stains the skin yellow. An alkali brought in contact with the yellow skin intensifies the color. Iodine in contact with the skin produces a yellowish to brown stain, much like that produced by nitric acid. The stain produced by nitric acid is intensified in color by an alkali, whereas that produced by iodine disappears, owing to the formation of a colorless iodide of the alkali.

Decomposition of nitric acid: It may be decomposed, with the elimination of water, as—

$$P_2O_5 + 6HNO_3 = 2H_3PO_4 + 3N_2O_5.$$

In this case the water eliminated combines with P_2O_5 to form H_3PO_4, phosphoric acid.

Action of the metals on nitric acid: The results produced by the action of the metals on nitric acid vary.

The metals may be arranged in five classes, according to their action on nitric acid, as follows:

1. Metals which have no action upon the acid, as the noble metals, gold, platinum, etc.

2. Metals which decompose the acid, with the formation of an oxide of the metal, water and nitrogen dioxide, N_2O_4, (nitrogen peroxide), for example, tin and antimony.

$$4HNO_3 + Sn = SnO_2 + 2H_2O + 2N_2O_4.$$

3. Metals which decompose the acid, with the formation of a nitrate of the metal, water and nitrous oxide, N_2O_3, for example, silver.

$$6HNO_3 + 4Ag = 4AgNO_3 + 3H_2O + N_2O_3.$$

4. Metals which decompose the acid, with the formation of a nitrate of the metal, water and nitrogen protoxide, N_2O_2, for example, copper.

$$8HNO_3 + 3Cu = 3Cu(NO_3)_2 + 4H_2O + N_2O_2.$$

5. Metals which decompose the acid, with the formation of a nitrate of the metal, water and hyponitrous oxide, N_2O, for example, zinc.

$$10HNO_3 + 4Zn = 4Zn(NO_3)_2 + 5H_2O + N_2O.$$

When very strong nitric acid acts upon zinc, ammonia, NH_3, is produced, which immediately combines with the excess of acid present to form ammonium nitrate.

$$9HNO_3 + 4Zn = 4Zn(NO_3)_2 + 3H_2O + NH_3.$$

The general method of preparing a nitrate of a metal is to treat the metal with nitric acid. Nitrates of all the metals are possible except the noble metals, and tin, antimony, etc.

All nitrates, except basic nitrates, are soluble in water. They undergo decomposition on the application of heat. Nitrates mixed with carbonaceous matter form mixtures which explode on the application of heat.

Example: Gunpowder, a mechanical mixture of a nitrate of an alkali, usually potassium nitrate, KNO_3, sulphur and powdered charcoal. When heat is applied, chemical change occurs with explosive violence. The reaction may be represented as follows:

$$2KNO_3 + C_3 + S = K_2S + 3CO_2 + N_2.$$

Action of nitric acid on organic substances: 1. Nitric acid may combine with an organic substance to form a nitrate.

2. It may act on an organic substance with the formation of a substitution product, as its action on cellulose, $C_6H_{10}O_5$, forming trinitro-cellulose, gun cotton, $C_6H_7(NO_2)_3O_5$, or on glycerin, $C_3H_8O_3$, forming trinitro-glycerin, $C_3H_5(NO_2)_3O_3$.

$$\underset{\text{Cellulose.}}{C_6H_{10}O_5} + 3HNO_3 = \underset{\text{Gun Cotton.}}{C_6H_7(NO_2)_3O_5} + 3H_2O.$$

$$\underset{\text{Glycerin.}}{C_3H_8O_3} + 3HNO_3 = \underset{\text{Nitroglycerin.}}{C_3H_5(NO_2)_3O_3} + 3H_2O.$$

3. It may completely destroy the organic matter.

Tests for nitric acid: *A*. In the free state (as nitric acid).

1. Nitric acid heated with slips of copper foil undergoes decomposition, with the production of nitrogen protoxide, N_2O_2, which latter, in contact with the oxygen of the air, forms brownish-red fumes of nitrous oxide, N_2O_3. The liquid, at the same time, assumes a greenish tint.

$$8HNO_3 + 3Cu = 3Cu(NO_3)_2 + 4H_2O + N_2O_2,$$
$$N_2O_2 + O = N_2O_3.$$

In case the nitric acid be present in small quantity, the reaction may be facilitated and rendered more delicate by the addition of sulphuric acid.

Delicacy of the test, 1 part of HNO_3 in 1000 parts of water.

2. When a solution of ferrous sulphate, $FeSO_4$, is carefully poured down the side of a test-tube containing a cooled mixture of nitric acid and concentrated sulphuric acid, a brown-colored ring or zone is formed immediately at the point of

junction of the two liquids. The brown coloration is due to the presence of $FeSO_4(NO)_2$. Heat destroys the dark color.

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + N_2O_2.$$

The liberated N_2O_2 ($2NO$) combines with a molecule of $FeSO_4$, forming the dark-colored compound $FeSO_4(NO)_2$.

$$FeSO_4 + N_2O_2 = FeSO_4(NO)_2.$$

Delicacy of the test, 1 part of HNO_3 in 10,000 parts of water.

3. Nitric acid added to brucine dissolved in concentrated sulphuric acid produces an intense red color. 1 part of brucine in 50,000 parts of water may be detected by this test.

4. Nitric acid is precipitated by cinchonamine sulphate, as a white crystalline precipitate—cinchonamine nitrate. 1 part of nitric acid in 500 parts of water may be detected by this test. 63 parts of nitric acid produce 359 parts of cinchonamine nitrate.

B. In combination (as a nitrate).

1. A nitrate heated with sulphuric acid and a slip of copper foil undergoes decomposition, with the production of brownish-red fumes of nitrous oxide, N_2O_3.

2. When a solution of ferrous sulphate is carefully poured down the side of a tube containing a cooled mixture of a solution of a nitrate and sulphuric acid, a brown-colored ring or zone is produced at the point of junction of the two liquids.

3. A solution of a nitrate, to which sulphuric acid has been added, when brought in contact with brucine, produces an intense blood-red color.

HYPONITROUS OXIDE, N_2O.

Molecular weight, 44.

44 grains measure 93.33 cubic inches. 44 grammes measure 22.32 litres. 1 litre weighs 1.971 grammes.

This gas is popularly known as nitrous oxide, or laughing gas.

Special history: Discovered by Priestley in 1776, who named it **dephlogisticated nitrous air.** Davy investigated it in 1799, and called it **nitrous oxide.**

Natural history: **It is not found in nature,** being wholly an artificially prepared compound.

Preparation: 1. By heating ammonium nitrate, NH_4NO_3, at a temperature of about 243° C. (470° F.).

$$\underset{\text{Molec. Wt. 80.}}{NH_4NO_3} = 2H_2O + \underset{\text{Molec. Wt. 44.}}{N_2O}.$$

80 parts by weight of ammonium nitrate furnish 44 parts by weight of hyponitrous oxide.

80 grains of NH_4NO_3 furnish 93.33 cubic inches of N_2O.
80 grammes " " 22.32 litres " "

On heating the ammonium nitrate it first fuses (at a temperature of 108° C.), and on heating to a higher temperature, about 243° C., undergoes decomposition, with the production of water and the evolution of hyponitrous oxide. If the temperature be above 260° C. (500° F.) other changes will occur, nitric oxide and nitrogen being evolved. In heating the NH_4NO_3, a temperature just sufficient to fuse the compound and cause the evolution of gas should be employed. If ammonium chloride be present, the hyponitrous oxide will be contaminated with chlorine. The gas prepared for inhalation should always be purified by being passed through two Woulff's bottles containing respectively solutions of sodium hydroxide, NaOH, and ferrous sulphate, $FeSO_4$. The sodium hydroxide removes acid vapors, and the ferrous sulphate removes nitrous oxide, N_2O_3.

The gas should be collected over warm water, as it is less soluble in warm than in cold water.

2. By the action of dilute nitric acid (specific gravity 1.2) on granulated zinc. This method is inferior to the one in which ammonium nitrate is employed.

$$10HNO_3 + 4Zn = 4Zn(NO_3)_2 + 5H_2O + N_2O.$$

Physical properties: A colorless, odorless gas having a sweet taste. Its specific gravity, compared with air, is 1.52. It is freely soluble in water. 100 volumes of water at a temperature of 15.5° C. (60° F.) absorb 78 volumes of the gas. It is liquefied under a pressure of 50 atmospheres at ordinary

temperature, under a pressure of 30 atmospheres at a temperature of 0° C., and under a pressure of 1 atmosphere at a temperature of —88° C. In the liquid state it has a specific gravity of 0.937. Liquid hyponitrous oxide blisters the skin when brought in contact with it. It is not combustible, but is a supporter of combustion, due to its decomposition into nitrogen and oxygen. A taper, charcoal, phosphorus, etc., burn in it as vividly as in an atmosphere of oxygen. It is necessary that the combustible body be burning freely when introduced, as otherwise the temperature will be insufficient to decompose the gas.

Hyponitrous oxide may be distinguished from oxygen as follows:

1. It does not form brownish-red fumes of nitrous oxide, N_2O_3, with nitrogen protoxide, N_2O_2.
2. It is not absorbed by an alkaline solution of pyrogallic acid.
3. It is much more soluble in water than oxygen.

Physiological properties: Its property of producing anæsthesia was first observed by Sir Humphry Davy, April 11, 1799, and was taken advantage of by him in having teeth extracted while under its influence. Because of its usually producing a condition of hilarity when inhaled, it was called "laughing gas."

No further mention of its use as an anæsthetic agent appears until 1844, when Dr. Wells, of Connecticut, found that persons under its influence felt no pain while undergoing surgical operations. Since then it has been generally employed in performing minor surgical operations, especially in relieving the pain incident to the extraction of teeth.

Ethyl ether was introduced as an anæsthetic by Dr. Morton in 1846, and chloroform by Dr. Simpson in 1847.

According to statistics, it is found that of the principal anæsthetics hyponitrous oxide is the safest, it having proved fatal only in 1 case in 300,000 cases in which it was administered, while ethyl ether has proved fatal in 1 case in 23,700 cases, and chloroform in 1 case in 2873 cases.

HYPONITROUS ACID, HNO.

This acid has never been isolated, it being known only in combination with a metal as a hyponitrite.

It is the oxyacid of hyponitrous oxide, but cannot be produced by the direct union of hyponitrous oxide and water, thus:

$$N_2O + H_2O = 2HNO.$$

It may be produced, in combination with a metal as a hyponitrite, by treating sodium nitrate with sodium amalgam, thus:

$$\overset{\text{Sodium Nitrate.}}{NaNO_3} + \overset{\text{Sodium Amalgam.}}{Na_4Hg} + 2H_2O = \overset{\text{Sodium Hyponitrite.}}{NaNO} + \overset{\text{Sodium Hydroxide.}}{4NaOH} + Hg.$$

On neutralizing the alkaline solution thus produced, with acetic acid, and adding argentic nitrate, a yellow precipitate of argentic hyponitrite, AgNO, is formed, thus:

$$\overset{\text{Sodium Hyponitrite.}}{NaNO} + AgNO_3 = NaNO_3 + AgNO.$$

NITROGEN PROTOXIDE, N_2O_2 or 2NO.

Molecular weight, 60. Specific gravity compared with hydrogen, 15. Therefore the molecular weight of the compound must be 30, and the molecular formula NO. 30 grammes of nitrogen protoxide measure 22.32 litres.

Its specific gravity compared with air is 1.039. The molecule consists of 1 volume of nitrogen and 1 volume of oxygen without condensation, otherwise its specific gravity would be double what it really is; thus,

Specific gravity of nitrogen, ...	0.972
" " oxygen, ...	1.105
" " the 2 volumes combined, .	2.077

$2.077 \div 2 = 1.0388$ = mean specific gravity of the two volumes. The observed specific gravity is 1.039.

Special history: It was known to Priestley in 1772. Davy determined its compound nature.

Natural history: It does not occur in nature, being produced wholly by artificial means.

Preparation: 1. By the action of dilute nitric acid on metallic copper.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + N_2O_2.$$

It is not obtained in a pure state by this method.

2. By decomposing potassium nitrate with ferrous sulphate in the presence of sulphuric acid.

$$\begin{aligned} &2KNO_3 + 6FeSO_4 + 4H_2SO_4 = \\ &3Fe_2(SO_4)_3 + K_2SO_4 + 4H_2O + N_2O_2. \end{aligned}$$

It is obtained in a pure state by this method.

Properties: A colorless gas. In contact with oxygen (air) it forms brownish-red fumes of nitrous oxide, N_2O_3, or of nitrogen dioxide, N_2O_4.

$$N_2O_2 + O = N_2O_3.$$

It is neither combustible nor a supporter of combustion. If, however, the combustible body, when introduced, be burning sufficiently energetically to effect the decomposition of the N_2O_2, combustion will take place. An ignited taper introduced into an atmosphere of N_2O_2 is immediately extinguished, because the temperature evolved in the combustion is not high enough to decompose the N_2O_2. On the other hand, if a piece of ignited phosphorus be introduced into the gas, the phosphorus continues to burn, because the temperature evolved in the combustion is high enough to decompose the N_2O_2 with the liberation of oxygen.

When an ignited taper is applied to a mixture of nitrogen protoxide, N_2O_2, and carbon disulphide, CS_2, combustion takes place with the production of an intensely white light.

Nitrogen protoxide is a neutral substance. It does not combine with the elements of water to form an acid.

It is employed as a test for free oxygen and to distinguish between the two gaseous supporters of combustion, hyponitrous oxide, N_2O, and oxygen. With hyponitrous oxide no change occurs, whilst with free oxygen brownish-red fumes of N_2O_3, or of N_2O_4 are produced.

NITROUS OXIDE, N_2O_3.

Molecular weight, 76.

Preparation: 1. By mixing four volumes of dry nitrogen protoxide, N_2O_2, with one volume of dry oxygen.

$$N_2O_2 + O = N_2O_3.$$

2. By the action of arsenious anhydride, As_2O_3, upon nitric acid.

$$As_2O_3 + 2HNO_3 = As_2O_5 + H_2O + N_2O_3.$$

Properties: A brownish-red gas, condensing at a temperature of —18° C. to a blue liquid.

It is capable of combining with the elements of water, if the water be ice-cold, to form an acid—nitrous acid, HNO_2.

$$N_2O_3 + H_2O = 2HNO_2.$$

The acid is very unstable. The addition of an excess of water at ordinary temperature decomposes it into nitric acid and nitrogen protoxide.

$$3N_2O_3 + H_2O = 2HNO_3 + 2N_2O_2.$$

Nitrous acid forms salts called nitrites.

$$\begin{aligned} HNO_2 + KOH &= \overset{\text{Potass. Nitrite.}}{KNO_2} + H_2O, \\ \text{or } N_2O_3 + 2KOH &= 2KNO_2 + H_2O. \end{aligned}$$

The nitrates of the fixed alkalies when heated give off oxygen and are reduced to nitrites.

$$KNO_3 = KNO_2 + O.$$

All nitrites are soluble in water. Argentic nitrite, $AgNO_2$, is the least soluble of the nitrites.

NITROGEN DIOXIDE, N_2O_4, or $2NO_2$.

Molecular weight, 92. Specific gravity compared with hydrogen, 23; hence the molecular formula is NO_2, molecular weight, 46.

Preparation: 1. By mixing four volumes of nitrogen, protoxide, N_2O_2, with two volumes of oxygen.

$$2NO + O_2 = N_2O_4 \text{ (or } 2NO_2\text{)}.$$

2. By heating dry plumbic nitrate, $Pb(NO_3)_2$.

$$2Pb(NO_3)_2 = 2PbO + 2N_2O_4 + O_2.$$

Properties: A brownish-red gas.

NITROGEN AND HYDROGEN.

Nitrogen and hydrogen under ordinary conditions have little affinity for each other, but under certain conditions enter into combination to form **ammonia,** NH_3.

AMMONIA, NH_3 (known as Ammoniacal Gas).

Molecular weight, 17. Specific gravity compared with hydrogen, 8.5. Specific gravity compared with air, 0.589. 17 grammes measure 22.32 litres.

It is the third lightest substance known, the first being hydrogen and the second marsh gas, CH_4.

It consists of 1 volume of nitrogen and 3 volumes of hydrogen condensed into 2 volumes.

Special history: Its combination as ammonium chloride, NH_4Cl (sal ammoniac), was known to Geber in the seventh century. Black, in 1756, studied its salts, and in 1790 Priestley obtained it in the gaseous state.

Natural history: It occurs in minute quantities in the air, especially after a thunder-storm, as ammonium nitrate NH_4NO_3, or as ammonium nitrite, NH_4NO_2. It is found in the soil as ammonium chloride. It is evolved in the decomposition of nitrogenous organic matter of animal origin in the presence of air and moisture.

Example:

$$\overset{\text{Urea.}}{CO(NH_2)_2} + H_2O = 2NH_3 + CO_2.$$

Iron, in rusting, decomposes the moisture of the air, the free hydrogen of which combines with atmospheric nitrogen to form ammonia.

Whenever nitrogenous organic matter, in which the nitrogen is not present as an oxide, is heated with a fixed alkali, ammoniacal gas is evolved.

Preparation: 1. Ammoniacal gas may be obtained by heating ordinary aqua ammoniæ.

$$NH_4OH = NH_3 + H_2O.$$

2. It may be obtained from any ammonium salt by heating it with a fixed alkali.

$$\overset{\text{Ammon. Chloride.}}{2NH_4Cl} + \overset{\text{Calcium Oxide.}}{CaO} = \overset{\text{Calcium Chloride.}}{CaCl_2} + H_2O + 2NH_3,$$

$$NH_4Cl + \overset{\text{Sodium Hydroxide.}}{NaOH} = \overset{\text{Sodium Chloride.}}{NaCl} + H_2O + NH_3.$$

3. By heating nitrogenous organic matter of animal origin with a fixed alkali.

4. By the destructive distillation of horn, coal, etc., in closed retorts. Most of the commercial ammonium salts are derived from the ammoniacal liquor produced in the destructive distillation of coal in making ordinary illuminating gas.

Properties: A colorless gas, having a pungent odor and strong alkaline properties.

It is not a supporter of combustion, and is only feebly combustible. In burning it, heat must be applied continuously from an outside source.

The oxidation of ammonia may be effected by introducing a hot platinum wire into a mixture of the gas with oxygen.

$$2NH_3 + O_3 = \overset{\text{Ammon. Nitrite}}{NH_4NO_2} + H_2O.$$

At a temperature of 10° C. (50° F.) the gas is condensed to a liquid under a pressure of 6 atmospheres. At a temperature of —40° C. (—40° F.) it is condensed to a liquid under a pressure of 1 atmosphere. The liquid boils at a temperature of —35° C. When ammonia passes from the liquid to the gaseous state cold is produced, and in passing from the gaseous to the liquid state heat is evolved. This property is made use of in producing ice artificially by means of ice machines. Liquid ammonia is first formed in suitable vessels, by condensing the gas, which liquid, in again becoming a gas, absorbs so much heat that the temperature of the brine surrounding the vessel containing the ammonia, is sufficiently reduced to convert into ice the water which is contained in the cans suspended in the brine.

The gas is exceedingly soluble in water. 1 volume of water at 0° C. (32° F.) absorbs 1050 volumes of the gas. 1 volume of water at 15° C. (59° F.) absorbs 727 volumes of the gas, this being about the strength of the stronger aqua ammoniæ of commerce.

The aqueous solution of ammoniacal gas is also called ammonium hydroxide, NH_4OH.

The amount of NH_3 absorbed by water depends upon the temperature of the water and the pressure exerted upon it. The lower the temperature of the water the more gas it will absorb. On passing the gas into water the latter increases in volume and decreases in density. Water at 50° F., saturated with the gas, has a specific gravity of 0.875, and contains 32.5 per cent. of NH_3.

Chemical relations of NH_3: It is a basic compound, capable of entering into combination to form salts.

1. It is capable of uniting directly with oxyacid radicals, thus:

$$2NH_3 + \overset{\text{Sulphuric Anhydride.}}{SO_3} = \overset{\text{Sulphamic Acid.}}{N_2H_6SO_3} \text{ (or } (NH_3)_2SO_3\text{).}$$

$$2.\quad 2NH_3 + \overset{\text{Carbon Dioxide.}}{CO_2} = \overset{\text{Ammon. Carbamate (Hypothetical).}}{N_2H_6CO_2}.$$

$$\overset{\text{Ammon. Carbamate.}}{N_2H_6CO_2} + H_2O = \overset{\text{Ammon. Carbonate.}}{(NH_4)_2CO_3}.$$

$$N_2H_6CO_2 - H_2O = \overset{\text{Carbamide (Urea).}}{CO(NH_2)_2}.$$

$$NH_3CO_2 = CO\left\{\begin{matrix} NH_2, \\ OH, \end{matrix}\right. \text{carbamic acid.}$$

True salts of NH_3: 1. Ammonia, NH_3, combines directly with acids to form salts without displacing the hydrogen of the acid.

$$NH_3 + HCl = \overset{\text{Ammonium Chloride.}}{NH_4Cl}.$$

$$2NH_3 + H_2SO_4 = \overset{\text{Ammonium Sulphate.}}{(NH_4)_2SO_4}.$$

Ammonia as a reagent: It precipitates many basic substances.

Example:

$$FeSO_4 + 2NH_4OH = Fe(OH)_2 + (NH_4)_2SO_4.$$

It precipitates all the metals except the alkalies and the alkaline earths—Ba, Sr, Ca, Mg—except when the latter are in concentrated solution.

Tests for ammonia: 1. Ammoniacal gas in contact with a glass rod moistened with hydrochloric acid produces white vapors of ammonium chloride.

2. If the gas be simply in aqueous solution, it may be recognized by its odor, especially on boiling the liquid.

3. If the ammonia be in combination as a salt, it may be detected by boiling the solution with sodium hydroxide and observing the odor of the evolved ammoniacal gas.

4. Nessler's test. Nessler's reagent is prepared by dissolving 25 grammes of potassium iodide in 100 c.c. distilled water and adding a saturated solution of mercuric chloride until the appearance of a slight permanent precipitate. 50 grammes of potassium hydroxide are added, and the whole diluted with distilled water to a volume of 250 c.c. The precipitate is allowed to subside, and the clear liquid decanted and preserved in well-stoppered bottles for use.

On the addition of Nessler's reagent to a solution containing ammonia, free or in combination, a brown coloration or a brown precipitate, dependent upon the quantity of ammonia present, will be formed.

$$\underbrace{2(KI)_2HgI_2}_{\text{Nessler's Reagent.}} + 3KOH + NH_3 = NHg_2I,H_2O + 7KI + 2H_2O.$$

17 parts of NH_3 will form 559 parts NHg_2I,H_2O.

5. Ammonia is precipitated by platinum chloride, $PtCl_4$, as ammonium platinic chloride, $(NH_4Cl)_2PtCl_4$.

CARBON, C.

Atomic weight, 12. Equivalent weight, 6. Valence, IV. Specific heat of graphite (carbon), 0.2. Its specific heat multiplied by its atomic weight $0.2 \times 12 = 2.4$. If its capacity for heat (0.467) at a temperature of 600° C. be multiplied by 12, the product is 5.604.

$$0.467 \times 12 = 5.604.$$

Special history: Carbon in the form of charcoal was known to the ancients.

In 1775, Lavoisier effected the combustion of the diamond in oxygen, and thus proved that the product of the combustion in oxygen of the diamond and of charcoal was identical, namely, carbon dioxide, CO_2. In 1790, Priestley established its elementary character.

Natural history: It is found in the three kingdoms of nature.

1. In the mineral kingdom it is found in coal and in native carbonates, etc., and in the atmosphere, as carbon dioxide, resulting from the respiration of animals, the combustion of carbonaceous substances, volcanic gases, etc.
2. Vegetable structures are largely composed of carbon in combination with other elements.
3. Animal tissues and products are largely composed of carbon.

Properties: Carbon is a solid, devoid of taste or odor, and, excepting the diamond, of a black color.

Carbon in all its forms is combustible in air or oxygen, yielding carbon dioxide as the sole product of its combustion. It is insoluble in every known liquid.

It crystallizes in two different forms, as octahedra and as hexagonal prisms, therefore **dimorphous.** In nature it occurs mostly in the amorphous condition.

Varieties of Carbon. 1. **Diamond:** The diamond crystallizes in cubes or in octahedra. It is the purest form of carbon and is the hardest substance known. It possesses the highest index of refraction of any substance known. When burned in oxygen, the sole product of the combustion is carbon dioxide. Usually a slight ash, consisting of mineral matter, remains.

2. **Graphite** (Plumbago, Black Lead): Graphite occurs in nature as a mineral.

In early times it was thought to be lead (black lead) because when drawn over paper it produced a streak similar to that produced by lead.

Scheele in 1779 proved that it was simply an allotropic form of carbon.

As found in nature it is contaminated with mineral matter. The purest specimen of graphite found contained from 95 per cent. to 96 per cent. of carbon, the remainder being mineral matter.

It is used in making lead pencils for writing purposes, and on account of its infusibility it is largely used in making crucibles. It is also used as a lubricating material for machinery.

3. **Coal.** Varieties:

1. Anthracite (contains the largest percentage of carbon).
2. Bituminous (contains less carbon than anthracite).
3. Cannel (contains less carbon than bituminous).

In addition to carbon, all coals contain mineral matter. Sulphur is a constituent of coal, partly in combination as ferric sulphide and partly as free sulphur.

4. **Wood charcoal**; Obtained by burning wood in a limited supply of air. It has the property of absorbing certain gaseous substances. One part of charcoal will absorb about 93 parts of ammoniacal gas. It possesses the property of absorbing certain solid substances, such as the alkaloids, from liquids.

5. **Animal charcoal**: Obtained by burning bones in a limited supply of air. It contains from 85 per cent. to 90 per cent. of mineral matter, chiefly calcium phosphate and calcium carbonate. It is largely used as a decolorizing agent, especially in decolorizing solutions of raw sugar in the refining of sugar.

6. **Coke**: Obtained by heating bituminous coal in closed iron retorts, an exit being provided for the escape of volatile matters. The higher the temperature to which the coal is subjected, the more dense the coke. In this process a deposition of carbon in an amorphous condition occurs on the sides of the hot retort. This amorphous carbon, known as gas-retort carbon, is exceedingly hard, and is sometimes employed for cutting glass. It is also used in making carbon pencils for the arc electric light.

7. **Lampblack:** Obtained by burning substances rich in carbon—such as resins, oils and natural gas—in a current of air insufficient for complete combustion.

Chemical properties: Carbon, under ordinary conditions, is an extremely inert substance. It enters into combination as a tetravalent element, *i. e.*, equivalent in saturating power to four atoms of hydrogen, as CH_4, CS_2, CO_2. In nature it is the transition element connecting the three kingdoms, animal, vegetable and mineral. It exists in the air (mineral kingdom), from which it is assimilated by plants (vegetable kingdom), and plants are consumed by animals (animal kingdom), and the carbon is finally returned by them as CO_2 in exhaled air to the atmosphere (mineral kingdom), thus completing the cycle of the three kingdoms.

COMPOUNDS OF CARBON AND OXYGEN.

The only compounds of carbon and oxygen are carbon monoxide, CO, and carbon dioxide, CO_2.

CARBON DIOXIDE, CO_2 (sometimes called Carbonic Acid).

Molecular weight, 44. Specific gravity compared with hydrogen, 22. Specific gravity compared with air, 1.524. 44 grammes measure 22.32 litres. 1 litre weighs 1.967 gramme. 1 cubic centimetre weighs 0.001967 gramme. 44 grains measure 93.33 cubic inches. It contains its own volume of oxygen, *i. e.*, 100 cubic inches of CO_2 contain 100 cubic inches of oxygen, the carbon being condensed within the oxygen.

Special history: Carbon dioxide was known in early times. It was examined by Black in 1757, and called by him "Fixed Air." In 1775, Lavoisier, experimenting on the products of the combustion of the diamond in oxygen, determined its exact nature and named it carbonic acid.

Natural history: It is present in the atmosphere in the proportion of 2 to 4 parts per 10,000 parts of air. It is contained in water, especially in the carbonated waters. Gaseous emanations from volcanoes contain it. It is found, in combination, as native carbonates, as calcium carbonate, magnesium carbonate, etc. Animals exhale it in the process of

dioxide, being a non-supporter of combustion and heavier than air, extinguishes a flame when poured upon it.

Physiological properties: Carbon dioxide taken into the stomach is harmless, but when inhaled acts as a direct poison. The undiluted gas causes death instantly by spasm of the glottis.

Air containing 12 to 14 per cent. of CO_2 produces giddiness, quickened circulation of the blood, fullness in the head, perhaps delirium, and finally coma, which may last some time.

Air containing 4 or 5 per cent. of the gas (such as air once breathed) produces a feeling of oppression with headache, and perhaps delirium or coma.

Air containing 3 per cent. of the gas produces considerable distress and may produce insensibility.

Air containing 1 or even 0.5 per cent. of the gas produces a drowsy feeling.

Its presence in the air to the extent of 0.1 per cent. may be considered the boundary line between good and bad air, it being understood that the carbon dioxide has been derived from the respiration of animals (see page 62).

Chemical properties: Dry carbon dioxide has no effect upon blue litmus paper. When the moist gas is brought in contact with blue litmus, the blue is changed to red.

With water it forms carbonic acid, H_2CO_3. This acid has never been isolated.

$$CO_2 + H_2O = H_2CO_3.$$

Carbonic acid combines with basic substances, forming carbonates of the bases.

$$H_2CO_3 + 2NaOH = Na_2CO_3 + 2H_2O.$$

One atom or both atoms of the hydrogen in carbonic acid may be replaced by a metal, forming two classes of salts, called respectively **acid** and **neutral carbonates,** thus:

$NaHCO_3$, acid sodium carbonate.
Na_2CO_3 neutral " "

Solubility of the carbonates: All carbonates are insoluble in water, except the carbonates of the alkalies, and the bicarbonates of the alkaline earths; therefore, if any soluble carbonate be added to a solution containing a salt of any metal other than an alkali, the metal will be precipitated as a carbonate.

Detection of carbon dioxide: The gas passed into a solution of barium hydroxide, $Ba(OH)_2$, or of calcium hydroxide, $Ca(OH)_2$, produces a white precipitate of barium or of calcium carbonate.

$$CO_2 + Ba(OH)_2 = \overset{\text{Barium Carbonate.}}{BaCO_3} + H_2O.$$

If the carbon dioxide be in combination as a carbonate, effervescence, due to the evolution of CO_2, will occur on treating the carbonate with an acid. The identity of the evolved gas may be proved by passing it into a solution of barium hydroxide or of calcium hydroxide.

The carbon dioxide in combination as a carbonate may be determined quantitatively in an apparatus devised for the purpose, consisting in general of a glass flask in which the carbonate is placed and another glass flask or receptacle to hold sulphuric acid. A weighed quantity of the carbonate is placed in one flask, a small quantity of water is added to it, sulphuric acid is placed in the other flask or receptacle, and the whole apparatus is weighed. The acid is now allowed to flow into the vessel containing the carbonate; decomposition of the carbonate occurs at once, with the evolution of carbon dioxide, which, before escaping from the apparatus, is dried by being obliged to pass through the unused portion of sulphuric acid in the apparatus. After the decomposition is completed, air is drawn through the apparatus to remove any carbon dioxide remaining in the flasks, and, after cooling, the whole apparatus is again weighed.

The loss in weight is due to the escape of the carbon dioxide evolved from the weight of carbonate decomposed.

CARBON MONOXIDE, CO (sometimes called Carbonic Oxide).

Molecular weight, 28. Specific gravity compared with hydrogen, 14. Specific gravity compared with air, 0.967. It contains half its volume of oxygen.

Special history: It was discovered by Priestley in 1796, who supposed it to be hydrogen. Its true nature was determined in 1803 by Cruickshank and others.

Natural history: Carbon monoxide is not found in nature except as an artificial product. It is found in the air in the neighborhood of brick or lime kilns or wherever there is an incomplete combustion of carbon (coal, charcoal, etc.). The gases issuing from blast furnaces, in the process of the reduction of the ores of iron, contain from 20 to 35 per cent. of carbon monoxide. The light blue flame produced in the burning of anthracite coal is due to the burning of carbon monoxide.

Preparation: 1. By passing carbon dioxide over red-hot carbon.

$$CO_2 + C = 2CO.$$

2. By passing carbon dioxide over red-hot iron.

$$4CO_2 + 3Fe = Fe_3O_4 + 4CO.$$

3. By heating oxalic acid or an oxalate with sulphuric acid.

$$\underset{\text{Oxalic Acid.}}{H_2C_2O_4} + H_2SO_4 = H_2O + H_2SO_4 + CO_2 + CO.$$

The CO_2 is separated from the CO by passing the mixed gases through a solution of sodium hydroxide contained in a Woulff's bottle. The CO_2 will be absorbed by the NaOH, forming sodium carbonate, while the CO passes unabsorbed.

4. By heating potassium ferrocyanide with sulphuric acid.

$$\underset{\text{Potass. Ferrocyanide.}}{K_4Fe(CN)_6} + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO.$$

5. By heating formic acid or a formate with sulphuric acid.

$$\underset{\text{Formic Acid.}}{CH_2O_2} + H_2SO_4 = H_2SO_4 + H_2O + CO.$$

Properties: A colorless, odorless gas. It is slightly soluble in water. 100 volumes of water at 60° F. dissolve 2.43 volumes of CO. It is combustible, burning with a pale blue and very hot flame. The product of its combustion is carbon dioxide. It is not a supporter of combustion.

Its critical point is —139° C., at which it liquefies under a pressure of 35.5 atmospheres. At a temperature of —190° C.

it liquefies under a pressure of 1 atmosphere, and at —210 °C. it liquefies in a vacuum.

It is one of the constituents, to the extent of about 34 per cent., of the illuminant called "water gas." Ordinary illuminating gas produced from the destructive distillation of bituminous coal contains from 3 to 7 per cent. of carbon monoxide.

It is an indifferent oxide, and enters into combination with very few substances. It has no effect upon red or blue litmus.

Physiological properties: It is a true narcotic poison. Its poisonous action is due to its property of forming a fixed compound with the hæmoglobin of the blood, namely, carbonic oxide hæmoglobin, $C_{636}H_{1025}N_{164}O_{189}FeS_3CO$, molecular weight 14,157. (See page 61.)

COMPOUNDS OF CARBON AND HYDROGEN.

The number of compounds of carbon and hydrogen is almost limitless.

Those compounds composed of only carbon and hydrogen are called hydro-carbons.

Two important compounds of carbon and hydrogen (hydrocarbons) are methane, CH_4 and ethene, C_2H_4.

METHANE, CH_4 (Marsh Gas; Light Carburetted Hydrogen; Fire-damp; Gas of the Acetates).

Molecular weight, 16. Specific gravity compared with hydrogen, 8. Specific gravity compared with air, 0.5576. It is the second lightest substance known.

16 grammes measure 22.32 litres. 1 litre weighs 0.713 gramme. 16 grains measure 93.33 cubic inches.

Special history: It was first examined by Volta in 1778. He obtained it by stirring the mud in marshes and collecting the gas (marsh gas) as it ascended through the water.

Natural history: Methane occurs in swamps or stagnant pools and wherever vegetable matter is undergoing decomposition out of contact with the air, but in the presence of moisture.

It is a constituent of the gases emanating from petroleum wells, and is also a constituent of the so-called "natural gas" largely used for heating purposes.

It occurs occluded in coal, and, escaping from it into the air of coal mines, constitutes the **fire-damp** of the miners.

Its origin in coal seams is supposed to be due to the action of water on coal (carbon).

$$C_2 + 2H_2O = CO_2 + CH_4.$$

Preparation: 1. By heating an acetate of an alkali with solid sodium hydroxide.

$$\overset{\text{Sodium Acetate.}}{NaC_2H_3O_2} \quad + \quad NaOH \quad = \quad \overset{\text{Sodium Carbonate.}}{Na_2CO_3} \quad + \quad \overset{\text{Methane.}}{CH_4}.$$

In preparing it by this method ordinary lime is usually added to the mixture to prevent the action of the caustic soda on the glass of the vessel in which the operation is conducted. It is, however, best performed in an iron instead of a glass retort.

2. By the action of nascent hydrogen on chloroform, $CHCl_3$.

$$CHCl_3 + 3H_2 = 3HCl + CH_4.$$

3. By passing steam over red-hot carbon (charcoal).

$$3C + 2H_2O = 2CO + CH_4.$$

4. By the destructive distillation of coal.

Properties: A colorless, odorless, tasteless gas. Sparingly soluble in water. 100 volumes of water at 0° C. (32° F.) absorb 5.4 volumes of the gas. It is combustible, burning with a pale luminous flame and the production of considerable heat. When mixed with twice its volume of oxygen and a flame or a spark is applied to the mixture, violent explosion occurs, with the production of water and carbon dioxide (the choke-damp or white damp of the miners).

$$CH_4 + 2O_2 = 2H_2O + CO_2.$$

Explosion is most violent on igniting a mixture composed of one volume of marsh gas with ten volumes of air.

Explosion occurs when a lighted taper is applied to a mixture of 1 volume of marsh gas with 15 volumes of air, and also in a mixture of 1 volume of marsh gas with only 6 volumes of air.

Chlorine combines with it, with explosive violence, when the mixture of the two gases is exposed to sunlight, forming, in the presence of moisture, carbon dioxide and hydrochloric acid.

$$CH_4 + 4Cl_2 + 2H_2O = CO_2 + 8HCl.$$

If the chlorine be present in great excess, it may substitute the hydrogen of the CH_4 with the production of carbon, tetrachloride, CCl_4, or lower derivatives, as $CHCl_3$, CH_2Cl_2, etc.

Chemical properties: It is a very inert gas, and does not form compounds except by substitution of its hydrogen.

ETHENE, C_2H_4 (Ethylene; Olefiant Gas; Heavy Carburetted Hydrogen).

Molecular weight, 28. Molecular volume, 2. Specific gravity compared with hydrogen, 14. Specific gravity compared with air, 0.978.

Special history: Discovered by Diemann, in 1795.

Natural history: It is present in natural gas and in the explosive gases of coal mines.

Preparation: 1. By the destructive distillation of bituminous coal, resins, oils and fats.

2. By the action of sulphuric acid on alcohol, C_2H_5OH, at a temperature of about 165° C. (329° F.). Sulphuric acid having a specific gravity of 1.580 boils at a temperature of 165° C., and, therefore, is well adapted for the purpose. Sulphuric acid of this specific gravity may be prepared by diluting 9 volumes of sulphuric acid of 1.842 specific gravity with 4 volumes of water. (The mixture will have a specific gravity of 1.581.)

Two reactions occur in the preparation of C_2H_4, by the action of sulphuric acid on alcohol at a temperature of 165° C. In the first reaction sulphovinic acid, $C_2H_5HSO_4$, is formed, which, on further heating, is immediately decomposed into ethene, C_2H_4, and sulphuric acid.

Ethene mixed with its own volume of chlorine and exposed to sunlight, forms an oily compound called dichlorethene, $C_2H_4Cl_2$.

ILLUMINATING GAS. COAL GAS.

Ordinary illuminating gas is produced by the destructive distillation of bituminous coal. Coal gas is a mixture consisting of illuminants, diluents and impurities. The chief illuminant is ethene (olefiant gas). The diluents are hydrogen, methane and carbon monoxide. The impurities are carbon dioxide, hydrogen sulphide and nitrogen.

Percentage Composition of a Crude Illuminating Gas:

Specific gravity of the gas, 0.532.

Hydrogen, H,	34.84
Methane, CH_4,	39.22
Ethene, C_2H_4, etc.,	8.74
Nitrogen, N,	3.08
Carbon dioxide, CO_2,	7.28
Carbon monoxide, CO,	6.72
Hydrogen sulphide, H_2S,	0.12
	100.00

The crude gas is purified by being passed through cylinders containing water, in which the solid and liquid impurities, as tar and water, are removed, and ammoniacal gas is absorbed. The gas is further purified by being passed through cylinders containing lime, which absorbs carbon dioxide and sulphur compounds.

FLAME.

On examining an ordinary flame—that of a candle, for instance—it is seen to consist of three concentric cones: the innermost, around the wick, appearing almost black, the next emitting a bright white light, and the outermost being so pale as to be almost invisible in daylight.

The dark, innermost cone consists merely of the gaseous combustible to which the air does not penetrate, and which is therefore not in a state of combustion.

In the second or luminous cone, combustion is taking place attended with the separation of carbon, which being in a state of incandescence confers luminosity upon this part of the flame.

In the pale, outermost cone perfect combustion is taking place, the separated carbon is completely consumed, because the supply of air in contact with the flame is unlimited.

In the flame of the blowpipe and also in the flame of the Bunsen burner, in both of which the combustible gas is mixed with a sufficient quantity of air before being burned, complete combustion of the carbon occurs, and therefore the flame is non-luminous.

When flame is cooled below the temperature at which combustion takes place, it is at once extinguished. The principle of the Davy miner's safety lamp depends upon the above fact. A Davy lamp may be carried into an explosive atmosphere, and although the combustible gas in the explosive atmosphere may burn within the wire gauze of the safety lamp with such energy as sometimes to heat the wire gauze to dull redness, the flame is not communicated to the explosive mixture outside.

CARBON AND NITROGEN.

CYANOGEN, CN.

Molecular formula, C_2N_2.

Cyanogen is sometimes represented by Cy, the abbreviation of the name. As represented by the formula CN, the sum of the atomic weights is 26, which is the specific gravity of the substance compared with hydrogen. This formula (CN) must be doubled in order to obtain a formula which will express a quantity of the compound twice its specific gravity compared with hydrogen; hence the molecule of cyanogen is expressed by the formula C_2N_2, and therefore the molecular weight of the compound is 52. Specific gravity compared with hydrogen, 26. Specific gravity compared with air, 1.801. 52 grammes measure 22.32 litres.

Special history: Compounds of this substance were known in early times. It was known in its combination as Prussian blue by Diesbach in 1704. Its combination with hydrogen as hydrocyanic acid, prussic acid, HCN, in solution, was discovered by Scheele in 1782. Gay-Lussac, in 1811, isolated its combination with hydrogen, as hydrocyanic acid in its anhydrous state, and in 1815 isolated cyanogen itself. Because it behaved as an elementary form of matter, Gay-Lussac believed it to be an element. Its compound nature was afterward proved, and it was then termed a "radical." It was the first radical discovered.

Natural history: It is not found in nature in the free state. It is contained in the gases issuing from blast furnaces. In the vegetable kingdom it is produced by the action of emulsin, a ferment, upon amygdalin, both being constituents of bitter almonds, peach kernels, etc.

$$\overset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \overset{\text{Oil of Bitter Almonds.}}{C_7H_6O} + \overset{\text{Hydrocyanic Acid.}}{HCN} + \overset{\text{Glucose.}}{2C_6H_{12}O_6}.$$

Preparation: 1. By heating dry mercuric cyanide, $Hg(CN)_2$.

$$Hg(CN)_2 = Hg + 2CN.$$

2. By heating potassium ferrocyanide with mercuric chloride.

$$\overset{\text{Potass. Ferrocyanide.}}{K_4Fe(CN)_6} + \overset{\text{Mercuric Chloride.}}{2HgCl_2} = 4KCl + Fe(CN)_2 + 4CN + Hg_2.$$

3. By the destructive distillation of ammonium oxalate.

$$\overset{\text{Ammon. Oxalate.}}{(NH_4)_2C_2O_4} = 4H_2O + 2CN.$$

Properties: A colorless gas, possessing the odor of bitter almonds. It is soluble in water, 1 volume of water at ordinary temperature absorbing 4 volumes of the gas. It is very soluble in alcohol. Its aqueous solution on standing undergoes decomposition with the formation of ammonium oxalate, thus:

$$4H_2O + 2CN = \overset{\text{Ammon. Oxalate.}}{(NH_4)_2C_2O_4}.$$

It liquefies at ordinary temperature under a pressure of 4 atmospheres, and at a temperature of —30° C. (—22° F.) it liquefies under a pressure of 1 atmosphere. It becomes solid at a temperature of —35° C. (—30° F.).

It is combustible, burning with a characteristic peach-blossom-colored flame.

Physiological properties: It is an intensely poisonous substance.

Chemical properties: It is an electro-negative radical, and therefore is capable of playing the part of an electro-negative element. In entering into combination chemically, it is analogous in its behavior to chlorine, iodine and bromine.

It will unite with a positive metal to form a cyanide.

$$K + CN = \overset{\text{Potass. Cyanide.}}{KCN}.$$

When passed into a solution of potassium hydroxide it produces potassium cyanide, potassium cyanate and water, thus:

$$2KOH + 2CN = \overset{\text{Potass. Cyanide.}}{KCN} + \overset{\text{Potass. Cyanate.}}{KCNO} + H_2O.$$

The cyanides are readily decomposed on the addition of an acid, with the production of hydrocyanic acid.

$$\overset{\text{Potass. Cyanide.}}{KCN} + HCl = KCl + \overset{\text{Hydrocyanic Acid.}}{HCN}.$$

All cyanides are insoluble in water, except the cyanides of the alkalies, the alkaline earths and mercuric cyanide.

If a carbonate of an alkali, for example, potassium carbonate, be heated, under appropriate conditions, with carbon (charcoal), the carbonate is reduced and metallic potassium separates, thus:

$$K_2CO_3 + 2C = K_2 + 3CO.$$

If a carbonate of an alkali be heated with nitrogenous organic matter, a cyanide of the alkali will be produced, thus:

$$K_2CO_3 + C + N_2 = \overset{\text{Potass. Cyanide.}}{2KCN} + O_3.$$

Ferrocyanogen: If a carbonate of an alkali and nitrogenous organic matter (horn, leather, etc.) be heated with iron filings and the fused mass be treated with boiling water, an electro-negative radical called ferrocyanogen, $Fe(CN)_6$, is produced, which enters into combination with the alkali to form a ferrocyanide.

$$\overset{\text{Potass. Cyanide.}}{6KCN} + Fe + O = \overset{\text{Potass. Ferrocyanide.}}{K_4Fe(CN)_6} + \overset{\text{Potass. Oxide.}}{K_2O}.$$

Hydroferrocyanic Acid: Potassium ferrocyanide, when treated with hydrochloric acid, is broken up into potassium chloride and **hydroferrocyanic acid.**

$$\overset{\text{Potass. Ferrocyanide.}}{K_4Fe(CN)_6} + 4HCl = \overset{\text{Hydroferrocyanic Acid.}}{H_4Fe(CN)_6} + 4KCl.$$

The four atoms of hydrogen in hydroferrocyanic acid are replaceable by a metal, therefore the radical ferrocyanogen, $Fe(CN)_6$, is tetravalent. The radical ferrocyanogen is sometimes represented by the abbreviation Cfy.

Potassium ferrocyanide (yellow prussiate of potash), $K_4Fe(CN)_6$, is employed as a reagent in testing for iron in combination as a ferric salt. With a ferric salt it produces a blue precipitate of ferric ferrocyanide (Prussian blue), $Fe_4(Fe(CN)_6)_3 = Fe_7(CN)_{18}$.

$$\overset{\text{Potass. Ferrocyanide.}}{3K_4Fe(CN)_6} + \overset{\text{Ferric Chloride.}}{2Fe_2Cl_6} = \overset{\text{Ferric Ferrocyanide. (Prussian Blue.)}}{Fe_4(Fe(CN)_6)_3} + 12KCl.$$

Potassium ferrocyanide has no action on ferrous salts.

Ferricyanogen: If chlorine be passed through a solution of potassium ferrocyanide, $K_4Fe(CN)_6$, it withdraws part of the potassium from the potassium ferrocyanide, producing a new radical, ferricyanogen, $Fe_2(CN)_{12}$, in combination as potassium ferricyanide (red prussiate of potash), $K_6Fe_2(CN)_{12}$.

Ferricyanogen is an electro-negative, hexavalent radical. The radical ferricyanogen is sometimes represented by the abbreviation Cdfy.

Ferricyanogen in combination is sometimes represented as a half molecule, as, for instance, with potassium, $K_3Fe(CN)_6$ instead of $K_6Fe_2(CN)_{12}$.

Hydroferricyanic Acid: Plumbic ferricyanide, when treated with sulphuric acid, is broken up into plumbic sulphate and **hydroferricyanic acid.**

$$\overset{\text{Plumbic Ferricyanide.}}{Pb_3Fe_2(CN)_{12}} + 3H_2SO_4 = \overset{\text{Plumbic Sulphate.}}{3PbSO_4} + \overset{\text{Hydroferricyanic Acid.}}{H_6Fe_2(CN)_{12}}.$$

Potassium ferricyanide is employed as a reagent in testing for iron in combination as a ferrous salt. With a ferrous salt

it produces a blue precipitate of ferrous ferricyanide (Turnbull's blue), $Fe_3Fe_2(CN)_{12}$.

$$\overset{\substack{\text{Potass.}\\ \text{Ferricyanide.}}}{K_6Fe_2(CN)_{12}} + \overset{\substack{\text{Ferrous}\\ \text{Sulphate.}}}{3FeSO_4} = \overset{\substack{\text{Ferrous Ferricyanide.}\\ \text{(Turnbull's Blue)}}}{Fe_3Fe_2(CN)_{12}} + \overset{\substack{\text{Potass.}\\ \text{Sulphate}}}{3K_2SO_4}.$$

Potassium ferricyanide has no action on ferric salts.

If potassium ferrocyanide be heated with sulphur, a radical called sulphocyanogen, CNS, is produced.

$$\overset{\substack{\text{Potass.}\\ \text{Ferrocyanide.}}}{K_4Fe(CN)_6} + 6S = \overset{\substack{\text{Potass.}\\ \text{Sulphocyanide.}}}{4KCNS} + \overset{\substack{\text{Ferrous}\\ \text{Sulphocyanide.}}}{Fe(CNS)_2}.$$

To convert all of the sulphocyanogen produced in the above reaction into potassium sulphocyanide, the solution of potassium and ferrous sulphocyanides is treated with potassium carbonate, which precipitates the iron as carbonate.

$$Fe(CNS)_2 + K_2CO_3 = 2KCNS + FeCO_3.$$

Hydrosulphocyanic Acid: Plumbic sulphocyanide when treated with hydrogen sulphide is broken up into plumbic sulphide and hydrosulphocyanic acid.

$$\overset{\substack{\text{Plumbic}\\ \text{Sulphocyanide.}}}{Pb(CNS)_2} + \overset{\substack{\text{Hydrogen}\\ \text{Sulphide.}}}{H_2S} = \overset{\substack{\text{Plumbic}\\ \text{Sulphide.}}}{PbS} + \overset{\substack{\text{Hydrosulphocyanic}\\ \text{Acid.}}}{2HCNS}.$$

Potassium sulphocyanide, KCNS, is employed as a delicate test for iron in combination as a ferric salt. With a ferric salt it produces an intense claret-red color, which color is destroyed on the addition of mercuric chloride. Meconic acid produces the same color with a ferric salt, but in the case of meconic acid the red color is not destroyed on the addition of mercuric chloride.

Cyanogen occurs in human saliva in combination as a sulphocyanide.

HYDROCYANIC ACID, HCN. (HCy.)

Molecular weight, 27. Molecular volume, 2. Specific gravity compared with hydrogen, 13.5. Specific gravity of the liquid acid at 7.2° C. compared with water, 0.705. Specific gravity of the liquid acid at 18° C., 0.696. It is one of the lightest liquids known, the lightest being cymogen, a petroleum product having a specific gravity of 0.59.

Special history: Hydrocyanic acid in aqueous solution was discovered by Scheele in 1782. In 1811 Gay-Lussac obtained it in its anhydrous condition.

Natural history: It is found in the aqueous distillate from cherry kernels, peach kernels, bitter almonds, etc. Its formation in these kernels is due to the action of the ferment, emulsin, upon the amygdalin of the kernel. It is contained in varying quantities in cherry brandy, "cherry bounce," etc.

Preparation: 1. By passing a stream of hydrogen sulphide over gently heated (temp. 30° C.) mercuric cyanide.

$$\overset{\substack{\text{Mercuric}\\\text{Cyanide.}}}{Hg(CN)_2} + \overset{\substack{\text{Hydrogen}\\\text{Sulphide.}}}{H_2S} = \overset{\substack{\text{Mercuric}\\\text{Sulphide.}}}{HgS} + \overset{\substack{\text{Hydrocyanic}\\\text{Acid.}}}{2HCN.}$$

2. By heating together chloroform and ammonia.

$$\overset{\text{Chloroform.}}{CHCl_3} + \overset{\text{Ammonia.}}{NH_3} = 3HCl + HCN.$$

3. By distilling potassium ferrocyanide with dilute sulphuric acid. (The best proportions are 10 parts of potassium ferrocyanide, 7 parts sulphuric acid and 14 parts of water.)

$$\overset{\substack{\text{Potass.}\\\text{Ferrocyanide.}}}{2K_4Fe(CN)_6} + \overset{\text{Sulphuric Acid.}}{3H_2SO_4} = \overset{\substack{\text{Potassium}\\\text{Ferro-ferrocyanide.}}}{K_2FeFe(CN)_6} + \overset{\substack{\text{Potass.}\\\text{Sulphate.}}}{3K_2SO_4} + \overset{\substack{\text{Hydrocyanic}\\\text{Acid.}}}{6HCN.}$$

4. By acting on a cyanide of a metal with an acid.

$$\overset{\substack{\text{Potass.}\\\text{Cyanide.}}}{KCN} + \overset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{HCl} = \overset{\substack{\text{Potass.}\\\text{Chloride.}}}{KCl} + \overset{\substack{\text{Hydrocyanic}\\\text{Acid.}}}{HCN.}$$

A two per cent. aqueous solution of hydrocyanic acid may be prepared by dissolving 100 grains of tartaric acid in two fluid-ounces of water and adding 44 grains of potassium cyanide.

Properties: Hydrocyanic acid, in its anhydrous state, is a colorless, highly volatile liquid possessing an odor of bitter almonds. It freezes at —17.8° C. (0° F.) and boils at 26.1° C. (79° F.). It mixes with water and alcohol in all proportions.

Both the pure acid and the aqueous solution decompose on standing (particularly when exposed to the light), with the separation of a brown substance called paracyanogen $(CN)_x$

and the production of ammonium oxalate and formate. A trace of mineral acid in the aqueous solution appears to retard the decomposition.

$$2CN + 4H_2O = \overset{\text{Ammon. Oxalate.}}{(NH_4)_2C_2O_4}.$$

$$HCN + 2H_2O = \overset{\text{Ammon Formate.}}{NH_4CHO_2}.$$

The aqueous solution of hydrocyanic acid, according to the United States Pharmacopœia, contains 2 per cent. of anhydrous hydrocyanic acid. As the acid in aqueous solution readily undergoes decomposition, the strength of the solution may be determined, when necessary, by precipitating the acid contained in a definite volume of the solution, as argentic cyanide by means of argentic nitrate, and calculating the quantity of hydrocyanic acid present from the weight of argentic cyanide obtained.

$$\overset{\text{Hydrocyanic Acid.}}{HCN} + \overset{\text{Argentic Nitrate.}}{AgNO_3} = \overset{\text{Argentic Cyanide.}}{AgCN} + \overset{\text{Nitric Acid.}}{HNO_3}$$

1 molecule of HCN furnishes 1 molecule of AgCN, or 27 parts of HCN (molecular weight of HCN = 27) furnish 134 parts of AgCN (molecular weight of AgCN = 134), therefore 1 part of HCN will furnish 4.96 parts of AgCN, thus:

$$27 : 134 :: 1 : 4.96.$$

Divide the weight of precipitate of AgCN obtained by 4.96, and the result will represent the amount of HCN present in the volume of HCN solution employed.

The quantity of HCN may also be calculated by the following proportion:

$$\overset{\text{AgCN.}}{134} : \overset{\text{HCN.}}{27} :: \text{wt. of prec. of AgCN obtained} : x.$$

The result will represent the amount of HCN present in the volume of HCN solution employed.

Chemical properties: Hydrocyanic acid is classed with the hydrogen acids. It is, possibly, the weakest acid known, its acid properties being so feeble that it cannot even displace carbonic acid from its compounds.

The hydrogen of hydrocyanic acid may be replaced by a metal to form a cyanide of the metal. In this respect it is analogous to hydrochloric acid.

$$HCN + KOH = KCN + H_2O.$$
$$HCl + KOH = KCl + H_2O.$$

All cyanides are insoluble, except the cyanides of the alkalies and alkaline earths and mercuric cyanide.

All cyanides are decomposed on the addition of an acid, with the production of hydrocyanic acid.

Physiological properties: It is one of the most deadly poisons known, and the most rapidly fatal, with possibly the single exception of nicotine. There are poisons which prove fatal when administered in smaller quantities, but none produce death so rapidly as hydrocyanic acid (except nicotine). It generally causes death in from a fractional part of a minute to five or fifteen minutes. $\frac{9}{10}$ of a grain of the acid has proved fatal. Antidote: cold effusion, and the breathing of diluted ammoniacal gas, or of chlorine.

The usual chemical antidote is a mixture of ferrous and ferric salts (ferrous sulphate, $FeSO_4$, and ferric chloride, Fe_2Cl_6), followed immediately by the administration of an alkaline carbonate (sodium carbonate, Na_2CO_3). The unabsorbed hydrocyanic acid is converted into insoluble Prussian blue, which may be removed from the stomach by means of an emetic, or the stomach pump. However, in cases of poisoning by hydrocyanic acid the results are so quickly fatal that death usually occurs before an antidote can be administered.

Detection of hydrocyanic acid. There are three principal tests, namely:

The silver test.
The iron test.
The sulphur test.

1. **The silver test:** (*a*) The hydrocyanic acid is precipitated by the addition of argentic nitrate. The precipitated argentic cyanide is dried and placed in a small glass ignition tube having a drawn-out extremity. The argentic cyanide in the tube is heated, and the cyanogen is given off as a gas,

which, when ignited at the drawn-out extremity of the tube, burns with a characteristic peachblossom-colored flame. Delicacy of the test, $\frac{1}{500}$ of a grain of hydrocyanic acid.

(*b*) The mouth of the glass jar or bottle containing the hydrocyanic acid is covered with an inverted watch glass in which has been previously placed a drop of argentic nitrate solution. Sooner or later, the vapor of the acid coming in contact with the argentic nitrate will produce microscopic prismatic crystals of argentic cyanide. If the acid be present in large quantity, the deposit will likely be mostly amorphous. No other substance known will, under similar conditions, produce a crystalline deposit with argentic nitrate. Delicacy of the test, $\frac{1}{1000000}$ of a grain of hydrocyanic acid. The identity of the crystals may be confirmed by applying the iron and sulphur tests.

2. **The iron test**: (*a*) The solution containing free hydrocyanic acid is rendered slightly alkaline with potassium hydroxide, which latter enters into combination with the acid to form potassium cyanide. A mixture of a ferrous and a ferric salt (ferrous sulphate and ferric chloride) is now added, followed by the addition of hydrochloric acid. A blue precipitate (Prussian blue) will appear, indicating the presence of a cyanide. Thus:

$$\overset{\text{Potass. Cyanide.}}{18KCN} + \overset{\text{Ferrous Sulphate.}}{3FeSO_4} + \overset{\text{Ferric Chloride.}}{2Fe_2Cl_6} =$$

$$\overset{\text{Potass. Sulphate.}}{3K_2SO_4} + \overset{\text{Potass. Chloride.}}{12KCl} + \overset{\text{Prussian Blue.}}{Fe_4(Fe(CN)_6)_3}.$$

(*b*) The iron test is also applicable for the detection of the vapor of hydrocyanic acid. The mouth of the vessel containing the acid is covered with an inverted watch glass in which has been previously placed a drop or two of potassium hydroxide. The alkali will absorb the vapor, with the formation of potassium cyanide. The drop of liquid on the watch glass is treated with a mixture of a ferrous and a ferric salt and then with hydrochloric acid, as above described. Prussian blue will appear. Delicacy of the test, $\frac{1}{10000}$ of a grain of hydrocyanic acid.

3. **The sulphur test:** (*a*) A few drops of yellow ammonium sulphide $(NH_4)_2S$ are added to the solution containing the hydrocyanic acid or cyanide, and the whole evaporated on a water bath almost to dryness. Should the residue posses a yellow color, it is moistened with a drop of water and again evaporated. This moistening with water and evaporating should be repeated until the yellow color of the residue is destroyed, except, possibly, a slight film of canary-yellow sulphur. (This procedure is necessary to drive off all of the ammonium sulphide, otherwise a black precipitate of sulphide of iron would be produced further on.) The cyanogen is now in combination with sulphur and ammonium as ammonium sulphocyanide, NH_4CNS. The cooled residue is dissolved in a drop or two of water and treated with a dilute solution of ferric chloride. A claret-red color will be produced, due to the formation of sulphocyanide of iron. Mercuric chloride destroys the color. Delicacy of the test, $\frac{1}{250000}$ of a grain of hydrocyanic acid.

(*b*) The sulphur test is also applicable for the detection of the vapor of hydrocyanic acid. A drop of ammonium sulphide is placed on a watch glass and inverted over the mouth of the vessel containing the hydrocyanic acid. After a time the watch glass is placed on a water bath and the liquid evaporated almost to dryness, etc., and then treated with a drop of dilute ferric chloride solution, as above described.

Delicacy of the test as thus applied (vapor), $\frac{1}{100000}$ of a grain of hydrocyanic acid.

SULPHUR. S.

Atomic weight, 32. Molecular weight, 64. Molecular volume (at 1000° C.), 2. Valence II, IV, VI. Below a temperature of 1000° C. the molecular volume is one-third the normal volume. Its specific gravity in the gaseous state, below a temperature of 1000° C., compared with hydrogen is 96. At a temperature above 1000° C. it suddenly expands and becomes normal as regards its specific gravity compared with hydrogen, namely, 32.

Its capacity for heat is 0.2. If its capacity for heat be multiplied by 32, the result will be 6.4, and therefore 32 is assumed to be the true atomic weight of sulphur. The specific gravity of sulphur compared with water is about 2.0.

Special history: Sulphur was known in the earliest times. It is mentioned in the Bible, in Genesis xix. 24, as brimstone.

Natural history: It is found widely distributed in nature, both as free sulphur and in combination.

In volcanic districts sulphur is found in the free state either in yellow crystals or in opaque amorphous masses.

It occurs in combination with hydrogen as hydrogen sulphide, H_2S, in springs of sulphuretted water. It also occurs in combination with metals as sulphides. Examples, ferric sulphide, FeS_2 (iron pyrites), plumbic sulphide, PbS (galenite), mercuric sulphide, HgS (cinnabar), etc.

It is found in combination as sulphates. Examples, calcium sulphate, $CaSO_4$ (gypsum), magnesium sulphate, $MgSO_4$ (Epsom salt), sodium sulphate, Na_2SO_4 (Glauber's salt), etc.

It is a constituent of many organic substances, both of vegetable and animal origin. Examples: substances of vegetable origin, gluten, vegetable albumin and the acrid volatile oils, as oil of mustard; substances of animal origin, albumin, fibrin, casein, muscular tissue, hair, etc. Hair contains from 4 to 5 per cent. of sulphur.

Preparation: 1. By melting out the sulphur from its impurities.

2. By distilling the sulphur in earthenware retorts and collecting the distilled sulphur in water. The sulphur thus obtained is redistilled in iron retorts, and the distilled sulphur collected either in cooled chambers constructed of brick (forming flowers of sulphur), or in water, from which it is afterwards taken and melted and cast into rolls (forming roll sulphur)

3. By the distillation of iron or copper pyrites in iron retorts.

Properties: The properties of sulphur differ according to the variety.

Varieties. Native sulphur, which occurs naturally in an amorphous condition or as octahedral crystals. It may be obtained in the form of octahedral crystals by the slow evaporation of a solution of sulphur in carbon disulphide.

Prismatic sulphur, obtained by fusing native sulphur and allowing it to crystallize.

Ductile sulphur, prepared by pouring melted sulphur heated to a temperature of about 800° F. into cold water.

Milk of sulphur (precipitated sulphur), obtained by precipitating the sulphur of an alkaline sulphide (polysulphide) with an acid.

$$K_2S_5 + 2HCl = 2KCl + H_2S + 4S.$$

Sulphur is found in commerce either as roll sulphur or as flowers of sulphur. It is dimorphous, *i. e.*, capable of crystallizing in two distinct forms, namely, octahedra and in oblique prisms. Ordinary sulphur as found in commerce is yellow, but the colors of its allotropic modifications are various. Native sulphur is somewhat transparent, whilst all the other forms are opaque. It is devoid of taste and odor.

Sulphur melts at a temperature of from 111° C. to 115° C. It vaporizes at 400° C., at which temperature its vapor density compared with hydrogen is 96. If heated to a temperature of 1000° C., its vapor density compared with hydrogen is 32.

Sulphur is insoluble in water, but soluble in turpentine, the fixed oils, petroleum ether (benzene), chloroform, ether, alcohol, and especially soluble in carbon disulphide.

Chemical properties: It unites with all the elements except nitrogen. Normally it is an electro-negative element, but it also acts as an electro-positive element.

It is electro-negative in its combination with hydrogen as hydrogen sulphide, H_2S. The **electro-negative** form is **soluble** in carbon disulphide.

It is electro-positive in its combination with oxygen as sulphurous anhydride, SO_2. The **electro-positive** form is **insoluble** in carbon disulphide.

Sulphur enters into combination with the metals to form sulphides, as plumbic sulphide, PbS.

COMPOUNDS OF SULPHUR AND OXYGEN.

Only three oxides of sulphur have thus far been isolated, namely:

SO_2, Sulphurous oxide or anhydride.
SO_3, Sulphuric oxide or anhydride.
S_2O_7, Hypersulphuric oxide or anhydride.

They are oxyacid radicals and are capable of forming oxyacids with the elements of water.

There are twelve oxyacids of sulphur, namely:

H_2SO_2, Hyposulphurous acid (this acid and its corresponding anhydride have never been isolated).
H_2SO_3, Sulphurous acid (corresponding anhydride, SO_2).
H_2SO_4, Sulphuric acid (" " SO_3).
$H_2S_2O_8$, Hypersulphuric acid (" " S_2O_7).
$H_2S_2O_3$, Thiosulphurous acid.
$H_2S_2O_4$, Thiosulphuric acid.
$H_2S_2O_7$, Disulphuric acid (not a distinct oxyacid).

Polythionic series:

$H_2S_2O_6$, Dithionic acid.
$H_2S_3O_6$, Trithionic acid.
$H_2S_4O_6$, Tetrathionic acid.
$H_2S_5O_6$, Pentathionic acid.
$H_2S_6O_9$, Hexathionic acid.

SULPHURIC ANHYDRIDE, SO_3.

Molecular weight, 80. Molecular volume, 2. Specific gravity compared with hydrogen, 40. Specific gravity in the solid state, compared with water, 1.95, in the liquid state, 1.97.

Natural history: Occurs in nature in combination in native sulphates; calcium sulphate, $CaSO_4 = CaO,SO_3$.

Preparation: 1. By passing a dry mixture of sulphurous anhydride and oxygen over red-hot platinized asbestos and collecting the resulting sulphuric anhydride in an ice-cold receiver.

$$\overset{\text{Sulphurous Anhydride.}}{SO_2} + O = \overset{\text{Sulphuric Anhydride.}}{SO_3}.$$

2. By distilling Nordhausen sulphuric acid and collecting the distillate in an ice-cold receiver.

$$\overset{\text{Nordhausen Sulphuric Acid.}}{H_2S_2O_7} = H_2SO_4 + SO_3.$$

3. By the action of heat on anhydrous sodium bisulphate.

$$\overset{\text{Sodium Bisulphate.}}{Na_2O(SO_3)_2} = \overset{\text{Sodium Sulphate.}}{Na_2SO_4} + SO_3.$$

4. By heating a mixture of sulphuric acid and phosphoric anhydride.

$$H_2SO_4 + \overset{\text{Phosphoric Anhydride.}}{P_2O_5} = \overset{\text{Metaphosphoric Acid.}}{2HPO_3} + SO_3.$$

Properties: Sulphuric anhydride is a white, odorless, crystalline substance. In appearance it resembles asbestos. It fuses at 18.3° C. (65° F.) and boils at 35° C. (95° F.).

Chemical properties: In the dry state it has no action on litmus, but with moisture it forms sulphuric acid, which latter immediately acts upon the litmus.

There are four hydrates of sulphuric anhydride, namely:

$H_2O(SO_3)_2 = H_2S_2O_7$, Nordhausen sulphuric acid.
$H_2OSO_3 = H_2SO_4$, Sulphuric acid (monohydrate).
$(H_2O)_2SO_3 = H_2SO_4,H_2O$, Glacial sulphuric acid (dihydrate).
$(H_2O)_3SO_3 = H_2SO_4,2H_2O$, Graham's sulphuric acid (trihydrate).

NORDHAUSEN SULPHURIC ACID, $H_2S_2O_7$.

Preparation: On exposing ferric sulphide, FeS_2 (iron pyrites), to the air, in the presence of moisture, oxidation occurs, and ferrous sulphate and sulphuric acid are formed.

$$\overset{\text{Ferric Sulphide.}}{FeS_2} + O_7 + 8H_2O = \overset{\text{Ferrous Sulphate.}}{FeSO_4,7H_2O} + H_2SO_4.$$

The ferrous sulphate is heated in contact with air, to drive off the 7 molecules of water of crystallization, and also to oxidize the ferrous sulphate to ferric sulphate.

$$\overset{\text{Ferrous Sulphate.}}{6FeSO_4} + 3O = \overset{\text{Ferric Sulphate.}}{2Fe_2(SO_4)_3} + \overset{\text{Ferric Oxide.}}{Fe_2O_3}.$$

The ferric sulphate is now heated at a high temperature in earthenware retorts, whereby it undergoes decomposition into ferric oxide and sulphuric anhydride, which latter distills over and is collected in a suitable vessel.

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

In the ferric sulphate which is heated in the retort, there is always a small quantity of water which distills over and combines with the SO_3, producing the liquid acid.

$$2SO_3 + H_2O = H_2S_2O_7.$$

Properties: Nordhausen sulphuric acid (called Nordhausen because it is prepared on a large scale in Nordhausen, a town in Saxony) is an oily liquid, having a specific gravity of 1.9, and as found in commerce is usually of a brownish color, owing to the presence of a minute quantity of organic matter. The acid has an intense affinity for moisture.

It is largely used in the process of dyeing, to dissolve indigo.

SULPHURIC ACID, H_2SO_4 (Oil of Vitriol).

Molecular weight, 98. Molecular volume, 4. Its observed specific gravity in the gaseous state, compared with hydrogen, is not one-half the molecular weight, 49, but 24.5. 98 grammes of H_2SO_4 in the gaseous state measure 44.64 litres, because, when the acid is heated to its point of vaporization, dissociation occurs, and one molecule of the acid breaks up into one molecule of H_2O and one molecule of SO_3, and as each of the latter molecules, expressed in grammes, in the gaseous state measures 22.32 litres, the combined volumes measure 44.64 litres.

Special history: Sulphuric acid was probably known to Geber in the seventh century. It is mentioned by Basil Valentine in the fifteenth century.

Natural history: In the mineral kingdom it is found in the free state, as a result of the oxidation of sulphur, in the so-called "vinegar springs" of volcanic districts. The Rio Vinagre, a river in South America, derives its name from the sour taste of the water, due to the presence of free sulphuric acid.

It is found in combination in native sulphates.

Preparation: By passing sulphurous anhydride, SO_2, vapors of nitric acid, HNO_3, steam, H_2O, and air into a leaden chamber, so arranged as to ensure their perfect admixture. The bottom of the chamber is covered with a thin layer of water.

The sulphurous anhydride is obtained by burning crude sulphur or pyrites in air.

The nitric acid is produced by the action of sulphuric acid on sodium nitrate.

The steam is derived from a steam boiler.

The air is provided in sufficient quantity by passing a constant current through the chamber.

Reactions concerned in the method: The nitric acid oxidizes the sulphurous anhydride, thereby converting it, in the presence of water, into sulphuric acid.

$$\overset{\text{Sulphurous Anhydride.}}{3SO_2} + \overset{\text{Nitric Acid.}}{2HNO_3} + \overset{\text{Water.}}{2H_2O} = \overset{\text{Sulphuric Acid.}}{3H_2SO_4} + \overset{\text{Nitrogen Protoxide.}}{N_2O_2}.$$

The nitrogen protoxide in the reaction immediately combines with oxygen from the air and becomes nitrogen tetroxide (dioxide), N_2O_4, which is again capable of converting fresh sulphurous anhydride into sulphuric acid.

$$\overset{\text{Nitrogen Protoxide.}}{N_2O_2} + O_2 = \overset{\text{Nitrogen Tetroxide.}}{N_2O_4}.$$

$$N_2O_4 + 2SO_2 + 2H_2O = 2H_2SO_4 + N_2O_2.$$

Thus, theoretically, a small quantity of nitric acid vapor, in the presence of air and moisture, will convert an indefinite quantity of sulphurous anhydride into sulphuric anhydride, the N_2O_2 merely acting as a carrier of oxygen to the sulphurous anhydride.

The acid thus obtained in the leaden chamber has a specific gravity of 1.55 and contains 64 per cent. of H_2SO_4. It is now evaporated in leaden pans until it has a specific gravity of 1.71, beyond which it would seriously corrode the leaden pans. It now contains 78 per cent. of H_2SO_4. It is further

concentrated by being heated in a platinum retort until the acid in the retort has a specific gravity of 1.842.

The sulphuric acid of 1.842 specific gravity has the composition $(H_2O)_{13}(SO_3)_{12}$. It freezes at —26° C. (—15° F.) and boils at 338° C. (640° F.).

On exposing the acid of 1.842 specific gravity to a freezing mixture, crystals separate which have the composition represented by the formula H_2SO_4, and which melt at a temperature of 10° C. (51° F.), and have a specific gravity of 1.848. This is considered the true monohydrate or H_2SO_4.

Glacial Sulphuric Acid, H_2SO_4, H_2O. (Dihydrate.)

Has a specific gravity of 1.780. Boils at 224° C. (435° F.)

Graham's Sulphuric Acid, H_2SO_4, $2H_2O$. (Trihydrate.)

Has a specific gravity of 1.632, and boils at a temperature of 175° C. (348° F.).

Properties: Sulphuric acid is an oily liquid, without odor, and, when pure, without color. As generally found in commerce, it is more or less brown in color, owing to the presence of organic matter. It is an intensely corrosive poison. It has a strong affinity for water, and when exposed to the air absorbs moisture from it and increases in volume and diminishes in specific gravity. In the laboratory it is largely used as a drying agent.

On account of its great affinity for moisture, it abstracts the elements of water from wood, leaving nothing but the carbon of the wood remaining. (The charring of wood by sulphuric acid)

It abstracts the elements of water from oxalic acid, thus:

$$\overset{\text{Oxalic Acid.}}{H_2C_2O_4} + H_2SO_4 = H_2SO_4 + H_2O + \overset{\text{Carbon Dioxide.}}{CO_2} + \overset{\text{Carbon Monoxide.}}{CO}.$$

It induces certain substances to assimilate the elements of water, as in the preparation of glucose from starch. (The acid used must be dilute.)

$$\overset{\text{Starch.}}{C_6H_{10}O_5} + H_2O + H_2SO_4 = \overset{\text{Glucose.}}{C_6H_{12}O_6} + H_2SO_4.$$

Impurities of Sulphuric Acid: Principally lead, derived from the leaden chambers, and arsenic, derived from arsenical pyrites used in the preparation of the acid.

Chemical properties: Sulphuric acid is one of the most powerful acids, and displaces all other acids from their compounds.

Behavior of the metals with Sulphuric Acid: The metals may be divided into three classes, according to their action on sulphuric acid, namely:

1. Those which have no action on the acid, as the noble metals, gold, platinum, etc.

2. Those which, at ordinary temperature, have no action on the acid, but act only on the application of heat, as copper.

$$\overset{\text{Copper.}}{Cu} + 2H_2SO_4 = \overset{\text{Cupric Sulphate.}}{CuSO_4} + 2H_2O + \overset{\text{Sulphurous Anhydride.}}{SO_2}.$$

3. Those which, when brought in contact with the acid, decompose it, with the evolution of hydrogen, as zinc.

$$\overset{\text{Zinc.}}{Zn} + H_2SO_4 = \overset{\text{Zinc Sulphate.}}{ZnSO_4} + H_2.$$

Sulphuric acid is a dibasic acid and forms two classes of salts, namely, acid sulphates, where only one atom of hydrogen of the acid is replaced by a metal, and normal sulphates, where both atoms of hydrogen are replaced by a metal.

Examples:

$NaHSO_4$, acid sodium sulphate.
Na_2SO_4, normal sodium sulphate.

All sulphates of the metals are soluble in water, except the sulphates of barium, calcium, strontium, lead, mercury and silver.

Detection of Sulphuric Acid: By acidifying the solution to be tested with nitric acid and adding a solution of barium chloride. Sulphuric acid or a sulphate produces with barium chloride a white precipitate of barium sulphate.

Every 233 parts of barium sulphate ($BaSO_4$ molecular weight = 233) are equivalent to 98 parts of H_2SO_4, or 80 parts of SO_3 (SO_3 molecular weight = 80). Therefore the equivalent in H_2SO_4 of a given quantity of precipitate of $BaSO_4$ may be determined by the proportion:

233 : 98 :: weight of precipitate of $BaSO_4$: $x = H_2SO_4$.

SULPHUROUS ANHYDRIDE, SO_2.

Molecular weight, 64. Molecular volume, 2. Specific gravity compared with hydrogen, 32. Specific gravity compared with air, 2.247. 64 grammes measure 22.32 litres.

Special history: The irritation produced in the human air passages by burning sulphur is mentioned by Homer and by Pliny. Its properties were investigated by Scheele and by Priestley, and the latter determined its true nature by burning sulphur in oxygen.

Natural history: It is found in the air of volcanic districts, and in the air of cities as a result of the oxidation of sulphur in burning coal.

Preparation: 1. By burning sulphur in air or oxygen.

$$S + O_2 = SO_2.$$

2. By bringing sulphuric acid in contact with red-hot carbon.

$$2H_2SO_4 + C = 2H_2O + CO_2 + 2SO_2.$$

3. By heating sulphuric acid with sulphur.

$$2H_2SO_4 + S = 2H_2O + 3SO_2.$$

4. By heating sulphuric acid with metallic copper.

$$\underset{\text{Copper.}}{Cu} + \underset{\text{Sulphuric Acid.}}{2H_2SO_4} = \underset{\text{Cupric Sulphate.}}{CuSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Sulphurous Anhydride.}}{SO_2}.$$

As sulphurous anhydride is very soluble in water, it therefore must be collected in dry bottles by displacement or over mercury.

Properties: A colorless gas, having a strong, suffocating, sulphurous odor. It is neither combustible nor a supporter of combustion. It is liquefied under a pressure of 2 to 3 atmospheres at ordinary temperature. At a temperature of —17.8° C. (0° F.) it liquefies under the ordinary atmospheric pressure. It boils at —10° C. (14° F.). It is soluble in water and alcohol. 1 volume of water at ordinary temperature absorbs about 40 volumes of the gas.

Sulphurous anhydride is a powerful bleaching agent. It does not destroy the coloring matter, but forms colorless compounds with it. Most of these colorless compounds are decomposed on exposure to direct sunlight, with the partial reappearance of the original color, as is frequently observed in straw goods which have been bleached by sulphurous anhydride.

It is used to prevent or arrest fermentation, especially to prevent fermentation in cider, for which purpose it is largely employed in its combination with calcium as calcium bisulphite, $CaSO_3,H_2SO_3$.

The gas is a valuable antiseptic and disinfectant.

It is a powerful reducing agent, owing to its tendency to become oxidized. It readily reduces arsenic acid to arsenious acid, thus:

$$\overset{\text{Arsenic Acid.}}{2H_3AsO_4} + \overset{\text{Sulphurous Anhydride.}}{2SO_2} + 2H_2O = \overset{\text{Sulphuric Acid.}}{2H_2SO_4} + \overset{\text{Arsenious Acid.}}{2H_3AsO_3}.$$

It reduces mercurous nitrate to metallic mercury.

$$\overset{\text{Mercurous Nitrate.}}{Hg_2(NO_3)_2} + SO_2 + 2H_2O = H_2SO_4 + \overset{\text{Nitric Acid.}}{2HNO_3} + \overset{\text{Mercury.}}{Hg_2}.$$

It does not reduce mercuric compounds.

Sulphurous anhydride in the presence of moisture decomposes hydrogen sulphide, with the formation of pentathionic acid and the separation of sulphur, thus:

$$\overset{\text{Sulphurous Anhydride.}}{5SO_2} + \overset{\text{Hydrogen Sulphide.}}{5H_2S} = 4H_2O + \overset{\text{Pentathionic Acid.}}{H_2S_5O_6} + \overset{\text{Sulphur.}}{S_5}.$$

SULPHUROUS ACID, H_2SO_3.

Water at ordinary temperature absorbs about 40 times its volume of sulphurous anhydride, forming a solution of sulphurous acid.

$$\overset{\text{Sulphurous Anhydride.}}{SO_2} + \overset{\text{Water.}}{H_2O} = \overset{\text{Sulphurous Acid.}}{H_2SO_3}$$

Sulphurous acid is a dibasic acid, one or both atoms of the hydrogen being replaceable by a metal, forming salts called, respectively, acid and normal sulphites, as,

$NaHSO_3$, acid sodium sulphite.
Na_2SO_3, normal sodium sulphite.

All sulphites are insoluble in water, except the sulphites of the alkalies and the bi-sulphites of the alkaline earths.

All sulphites, under ordinary conditions, are decomposed on the addition of a stronger acid, with the formation of a salt of the acid added, water, and the evolution of sulphurous anhydride, thus:

$$\overset{\text{Sodium Sulphite.}}{Na_2SO_3} + \overset{\text{Hydrochloric Acid.}}{2HCl} = \overset{\text{Sodium Chloride.}}{2NaCl} + \overset{\text{Water.}}{H_2O} + \overset{\text{Sulphurous Anhydride.}}{SO_2}.$$

THIOSULPHUROUS ACID, $H_2S_2O_3$ (formerly called Hyposulphurous Acid).

The free acid has never been isolated. It is known only in combination with a metal as a salt—a thiosulphite.

The salts of thiosulphurous acid are prepared by boiling a solution of a sulphite with sulphur, thus:

$$\overset{\text{Sodium Sulphite.}}{Na_2SO_3} + S = \overset{\text{Sodium Thiosulphite.}}{Na_2S_2O_3}.$$

The thiosulphites are decomposed on the addition of a stronger acid, with the formation of a salt of the acid added, water, the evolution of sulphurous anhydride and the separation of sulphur, thus:

$$\overset{\text{Sodium Thiosulphite.}}{Na_2S_2O_3} + \overset{\text{Hydrochloric Acid.}}{2HCl} = \overset{\text{Sodium Chloride.}}{2NaCl} + \overset{\text{Water.}}{H_2O} + \overset{\text{Sulphurous Anhydride.}}{SO_2} + \overset{\text{Sulphur.}}{S}.$$

Sodium thiosulphite (formerly called sodium hyposulphite) is largely used in photography to dissolve argentic chloride, thus:

$$\overset{\text{Argentic Chloride.}}{2AgCl} + \overset{\text{Sodium Thiosulphite.}}{3Na_2S_2O_3} = \overset{\text{Sodium Chloride.}}{2NaCl} + \overset{\text{Soluble Argentic Sodic Thiosulphite.}}{Ag_2S_2O_3(Na_2S_2O_3)_2}.$$

Sodium thiosulphite is employed in analytical chemistry to separate aluminium from iron. Aluminium is precipitated by the thiosulphite as aluminium oxide, while the iron remains in the solution unchanged, thus:

$$\overset{\text{Aluminium Sulphate.}}{Al_2(SO_4)_3} + \overset{\text{Sodium Thiosulphite.}}{3Na_2S_2O_3} = \overset{\text{Sodium Sulphate.}}{3Na_2SO_4} + \overset{\text{Aluminium Oxide.}}{Al_2O_3} + \overset{\text{Sulphurous Anhydride.}}{3SO_2} + \overset{\text{Sulphur.}}{3S}.$$

Sodium thiosulphite in the presence of iodine forms sodium iodide and sodium tetrathionate, thus:

$$\overset{\text{Sodium Thiosulphite.}}{2Na_2S_2O_3} + \overset{\text{Iodine.}}{I_2} = \overset{\text{Sodium Iodide.}}{2NaI} + \overset{\text{Sodium Tetrathionate.}}{Na_2S_4O_6}.$$

HYPOSULPHUROUS ACID, H_2SO_2.

Preparation: By acting on zinc with sulphurous acid.

$$\overset{\text{Sulphurous Acid.}}{H_2SO_3} + \overset{\text{Zinc.}}{Zn} = \overset{\text{Zinc Oxide.}}{ZnO} + \overset{\text{Hyposulphurous Acid.}}{H_2SO_2}.$$

It combines with metals to form salts called hyposulphites.

DITHIONIC ACID, $H_2S_2O_6$.

Preparation: By the action of sulphurous anhydride on manganese dioxide in suspension in cold water.

$$2SO_2 + MnO_2 = MnS_2O_6.$$

The MnS_2O_6 (manganous dithionate) is treated with barium sulphide.

$$MnS_2O_6 + BaS = MnS + BaS_2O_6,$$

and the barium dithionate, BaS_2O_6, is finally treated with just sufficient sulphuric acid to liberate the dithionic acid.

$$BaS_2O_6 + H_2SO_4 = BaSO_4 + \overset{\text{Dithionic Acid.}}{H_2S_2O_6}.$$

Properties: A colorless, odorless liquid having a specific gravity of 1.347.

HYDROGEN AND SULPHUR.

HYDROGEN SULPHIDE, H_2S. (Sulphuretted Hydrogen.)

Molecular weight, 34. Molecular volume, 2. Specific gravity compared with hydrogen, 17. Specific gravity compared with air, 1.1912. 34 grammes measure 22.32 litres. 34 grains measure 93.33 cubic inches.

Special history: It was known in early times. Scheele, in 1777, first pointed out its constituents.

Natural history: Hydrogen sulphide is found in volcanic gases and in certain mineral waters—sulphuretted waters. It occurs in the gases resulting from the putrefaction of organic substances containing sulphur, particularly in the gases resulting from the putrefaction of organic substances of animal origin. Hydrogen sulphide is formed when the white of egg (albumin, a substance containing sulphur) undergoes decomposition. The blackening of a silver spoon by the contents of an egg is due to the action of hydrogen sulphide, and indicates that the egg has undergone more or less decomposition.

Preparation: 1. By decomposing a sulphide with an acid.
(*a*) The action of dilute sulphuric acid on ferrous sulphide.

$$\overset{\text{Ferrous Sulphide.}}{FeS} + \overset{\text{Sulphuric Acid.}}{H_2SO_4} = \overset{\text{Ferrous Sulphate.}}{FeSO_4} + \overset{\text{Hydrogen Sulphide.}}{H_2S.}$$

Hydrogen sulphide prepared from ferrous sulphide may contain impurities, and consequently should be washed by being passed through a Woulff's bottle containing water before being used in delicate experiments.

(*b*) The action of hot dilute hydrochloric acid on antimonious sulphide. H_2S prepared by this method is pure.

$$\overset{\text{Antimonious Sulphide.}}{Sb_2S_3} + \overset{\text{Hydrochloric Acid.}}{6HCl} = \overset{\text{Antimonious Chloride.}}{2SbCl_3} + \overset{\text{Hydrogen Sulphide.}}{3H_2S.}$$

Properties: Hydrogen sulphide is a colorless gas, having an odor somewhat similar to the odor of rotten eggs. It is freely absorbed by water. Water at 15° C. (59° F.) absorbs 3.23 times its volume of the gas. It is a poisonous gas. Under a pressure of 17 atmospheres it is liquefied at ordinary temperature. At a temperature of —74° C. (—101° F.) it becomes liquid at ordinary pressure. It is combustible, burning with a pale blue flame. It has acid properties, and is classed with the hydrogen acids. Certain metals are directly capable of displacing the hydrogen of the compound, with the formation of a sulphide of the metal. Thus:

$$\overset{\text{Silver.}}{Ag_2} + H_2S = \overset{\text{Argentic Sulphide.}}{Ag_2S} + H_2.$$

All sulphides are insoluble except the sulphides of the alkalies and the alkaline earths.

Hydrogen sulphide is used in the laboratory as a reagent to precipitate the metals of the second group.

The colors of the various sulphides produced by hydrogen sulphide are, in many cases, characteristic and serve as important tests.

Examples:

Antimonious sulphide, Sb_2S_3, orange red.
Arsenious sulphide, As_2S_3, yellow.
Cupric sulphide, CuS, black.
Cadmium sulphide, CdS, yellow.
Zinc sulphide, ZnS, white.

CARBON AND SULPHUR.

CARBON DISULPHIDE, CS_2.

Preparation: By passing the vapor of sulphur over red-hot carbon (charcoal).

$$C + S_2 = CS_2.$$

Its principal use is as a solvent for caoutchouc (rubber), sulphur and phosphorus.

PHOSPHORUS. P.

Atomic weight, 31. Specific gravity compared with hydrogen, 62. Its capacity for heat (0.21) multiplied by its atomic weight (31) gives a result of 6.51. $0.21 \times 31 = 6.51$. Atomic volume, ½. Molecular weight, 124. Valence III, V.

Special history: Discovered by Brandt, in 1669, in urine. Gahn, in 1768, discovered phosphorus in bones (present as calcium phosphate, $Ca_3(PO_4)_2$), and in 1769 Scheele devised a method by which it could readily be obtained from bones. Its elementary character was determined in 1810–1812 by Davy, Gay-Lussac and others.

Natural history: It is never found in nature in the free state, but always in combination. It is widely distributed in nature as native phosphates, principally as calcium phosphate, $Ca_3(PO_4)_2$. It is a constituent, in small quantity, of vegetable structures and animal tissues

spontaneous combustion of the phosphorus will take place. This latter occurs because of the finely divided condition of the phosphorus.

Phosphorus occurs in four varieties, namely: 1. Clear, transparent variety.

A soft, yellow, wax-like substance, having a garlic-like odor. Specific gravity, 1.84. This is the ordinary variety usually found in commerce in the form of sticks.

2. White, opaque variety.

This variety is formed by the action of light on the yellow variety when kept under water. It appears as a white crust on the sticks of the yellow variety. Specific gravity, 1.51.

3. Black variety.

Produced by melting the ordinary phosphorus and suddenly cooling it to 0° C. (32° F.).

4. Red variety.

Produced by heating yellow phosphorus at a temperature of about 238° C. (460° F.) for 30 or 40 hours in an atmosphere of carbon dioxide or in any gas free from substances that will oxidize the phosphorus. It is an amorphous body and of a dull red or maroon color, without taste and odor. Specific gravity, 2.17. Its firing point is 316° C. (600° F.). It is insoluble in carbon disulphide. By the action of heat, in the presence of air, it is changed back to the yellow variety. It is permanent in the air and gives off no vapor.

Both the yellow and red varieties of phosphorus are extensively used in making lucifer matches. The material on the so-called safety matches is composed of red phosphorus intimately mixed with substances that readily give up their oxygen, such as the following mixture:

Potassium Chlorate,	$KClO_3$,	32	parts.
Potassium Bichromate,	$K_2Cr_2O_7$,	12	"
Red Lead,	Pb_3O_4,	32	"
Antimonious Sulphide,	Sb_2S_3,	24	"

Physiological properties: All the varieties of phosphorus, with the exception of the red variety are poisonous. The vapors, when inhaled, produce necrosis of the jaw-bone. Necrosis of the jaw-bone is, consequently, a common disease

in persons who are engaged in making lucifer matches. The red, non-poisonous variety, which gives off no vapor at ordinary temperature, is now largely used in match making, thereby considerably lessening the danger of necrosis in the workmen.

The symptoms of phosphorus poisoning are often long delayed, sometimes not appearing for many hours or even days. In the most rapidly fatal case reported, death occurred in 12 hours; in the most prolonged case it occurred in 12 days.

$\frac{1}{8}$ of a grain has proved fatal in an adult.
$\frac{1}{50}$ " " " a child.

Antidote, a dilute solution of cupric sulphate.

Phosphorus, in combination as phosphates, phosphites and hypophosphites, is largely used in medicine.

Detection of uncombined phosphorus: 1. Mitscherlich's test.

Consists in distilling the substance containing the free phosphorus with diluted sulphuric acid, and conducting the evolved vapors through a glass tube surrounded by a glass Liebig's condenser. The vapor of phosphorus is thus condensed, and gives rise to a continuous luminosity when observed in the dark.

By this method $\frac{1}{50}$ of a grain of phosphorus in 2000 fluid grains of water has been recognized. In this case the luminosity continued during 34 minutes, and therefore the amount of phosphorus that passed through the tube per second must have been something less than the $\frac{1}{100000}$ part of a grain; yet this was even more than sufficient to identify the phosphorus with absolute certainty.

2. Hydrogen method.

Is based upon the property possessed by free phosphorus, and the lower oxides of phosphorus, of forming, with nascent hydrogen, hydrogen phosphide, H_3P, which burns with a greenish flame.

3. Phosphide of silver method.

The substance containing free phosphorus is distilled with dilute sulphuric acid, as in Mitscherlich's method, except that a stream of carbon dioxide is continuously passed through the apparatus, and the vapor of phosphorus is conducted into a solution of argentic nitrate, with which it forms insoluble argentic phosphide. The argentic phosphide is collected and washed on a filter which has been previously washed with dilute nitric acid and water; it is then suspended in a little water and placed in the hydrogen apparatus as in the hydrogen method. The argentic phosphide is decomposed in the presence of nascent hydrogen, with the formation of hydrogen phosphide, H_3P, which burns with a green flame.

COMPOUNDS OF PHOSPHORUS AND OXYGEN.

P_2O, Hypophosphorous oxide or anhydride (has never been isolated).

P_2O_3, Phosphorous oxide or anhydride.

P_2O_5, Phosphoric " "

All of these anhydrides form acids with the elements of water.

$P_2O + 3H_2O = 2H_3PO_2$, Hypophosphorous acid.
$P_2O_3 + 3H_2O = 2H_3PO_3$, Phosphorous acid.
$P_2O_5 + 3H_2O = 2H_3PO_4$, Orthophosphoric acid.

PHOSPHORIC ANHYDRIDE, P_2O_5.

Molecular weight, 142. Occurs in nature in combination as phosphates.

Preparation: By burning phosphorus in dry oxygen or air.

$$P_2 + O_5 = P_2O_5.$$

Properties: A white, flaky solid. It has an intense affinity for moisture, and therefore rapidly deliquesces in the air.

Phosphoric anhydride enters into combination with the elements of one, two or three molecules of water, forming acids, as follows:

$$P_2O_5 + \begin{cases} H_2O = 2HPO_3, & \text{Metaphosphoric acid.} \\ 2H_2O = H_4P_2O_7, & \text{Pyrophosphoric acid.} \\ 3H_2O = 2H_3PO_4, & \text{Orthophosphoric acid (the common phosphoric acid).} \end{cases}$$

Preparation of the three acids formed by P_2O_5 with the elements of H_2O.

1. **Metaphosphoric acid,** HPO_3. (Glacial phosphoric acid.)

(*a*) By dissolving phosphoric anhydride in water.

$$P_2O_5 + H_2O = 2HPO_3.$$

(*b*) By heating phosphorus with strong nitric acid, evaporating to dryness and strongly heating the residue.

$$P_6 + 10HNO_3 = 10NO + 2H_2O + 6HPO_3.$$

2. **Pyrophosphoric acid,** $H_4P_2O_7$.

By heating orthophosphoric acid to 215° C. (419° F.).

3. **Orthophosphoric acid,** H_3PO_4.

By heating phosphorus with dilute nitric acid.

$$P_6 + 10HNO_3 + 4H_2O = 10NO + 6H_3PO_4.$$

The three acids may be distinguished from one another by their behavior with .albumin, argentic nitrate and barium chloride.

	WITH ALBUMIN.	WITH ARGENTIC NITRATE.	WITH BARIUM CHLORIDE.
Metaphosphoric acid.	Coagulates.	White, gelatinous precipitate ($AgPO_3$).	White precipitate.
Pyrophosphoric acid.	No action.	No precipitate, unless the solution is rendered alkaline, when a *white* precipitate ($Ag_4P_2O_7$), is produced.	No precipitate, unless the solution is slightly alkaline, when a white precipitate is produced.
Orthophosphoric acid.	No action.	No precipitate, unless the solution is rendered alkaline, when a yellow precipitate (Ag_3PO_4), is produced.	No precipitate, unless the solution is slightly alkaline, when a white precipitate is produced.

One, two or all three atoms of hydrogen in orthophosphoric acid may be replaced by metals, forming three classes of salts.

Examples: 1. NaH_2PO_4, dihydrogen sodic phosphate.

2. Na_2HPO_4, disodic hydrogen phosphate (ordinary sodium phosphate).

3. Na_3PO_4, trisodic phosphate.

The hydrogen atoms may be replaced by elements differing in kind, as:

$NaNH_4HPO_4$, sodium ammonium phosphate (microcosmic salt).

$MgNH_4PO_4$, magnesium ammonium phosphate.

Magnesium ammonium phosphate when strongly heated breaks up into magnesium pyrophosphate, water and ammoniacal gas.

$$\overset{\substack{\text{Magnesium}\\ \text{Ammon. Phosphate.}}}{2MgNH_4PO_4} = \overset{\substack{\text{Magnesium}\\ \text{Pyrophosphate.}}}{Mg_2P_2O_7} + \overset{\text{Water.}}{H_2O} + \overset{\text{Ammonia.}}{2NH_3}.$$

All four atoms of hydrogen in pyrophosphoric acid are replaceable by a metal, as:

$Mg_2P_2O_7$, magnesium pyrophosphate.

The one atom of hydrogen in metaphosphoric acid is replaceable by a metal, as:

$NaPO_3$, sodium metaphosphate.
$Ca(PO_3)_2$, calcium metaphosphate.
Orthophosphoric acid is tribasic.
Pyrophosphoric acid is tetrabasic.
Metaphosphoric acid is monobasic.

PHOSPHOROUS ANHYDRIDE, P_2O_3.

Molecular weight, 110.

Preparation: By burning phosphorus in a limited supply of air.

Properties: A white, flaky, non-crystalline substance. It is very volatile, emitting a garlic-like odor.

PHOSPHOROUS ACID, H_3PO_3.

Preparation: By adding phosphorus trichloride to water.

$$\overset{\substack{\text{Phosphorus}\\ \text{Trichloride.}}}{PCl_3} + \overset{\text{Water.}}{3H_2O} = \overset{\substack{\text{Hydrochloric}\\ \text{Acid.}}}{3HCl} + \overset{\substack{\text{Phosphorous}\\ \text{Acid.}}}{H_3PO_3}.$$

It enters into combination with metals to form phosphites. It is dibasic, only two of the three atoms of hydrogen in the acid being replaceable by a metal, as:

Na_2HPO_3.
NaH_2PO_3.
$CaHPO_3$.

HYPOPHOSPHOROUS ANHYDRIDE, P_2O.

This anhydride has never been isolated. It is known only in combination.

In combination with the elements of water it forms hypophosphorous acid.

$$P_2O + 3H_2O = 2H_3PO_2.$$

HYPOPHOSPHOROUS ACID, H_3PO_2.

Preparation: By heating phosphorus with a strong solution of barium hydroxide, and decomposing the barium hypophosphite produced by means of sulphuric acid, which sets the acid free.

Properties: A thick liquid having a strong acid reaction.

Hypophosphorous acid forms a class of salts called hypophosphites.

Hypophosphorous acid is monobasic, only one of the atoms of hydrogen in the acid being replaceable by a metal, as,

NaH_2PO_2, Sodium hypophosphite.
$Ca(H_2PO_2)_2$, Calcium hypophosphite.

HYDROGEN PHOSPHIDE, H_3P. (Phosphoretted Hydrogen.)

Molecular weight, 34. Molecular volume, 2. Specific gravity compared with hydrogen, 17. Specific gravity compared with air, 1.19.

Natural history: Evolved in the putrefaction of organic substances containing phosphorus.

Preparation: By boiling phosphorus in a strong solution of a fixed alkali, thus:

$$\overset{\text{Phosphorus.}}{P_4} + \overset{\text{Potass. Hydroxide.}}{3KOH} + \overset{\text{Water.}}{3H_2O} = \overset{\text{Potass. Hypophosphite.}}{3KH_2PO_2} + \overset{\text{Hydrogen Phosphide.}}{PH_3}.$$

Properties: A colorless gas having an odor similar to that produced by putrefying fish.

The gas as ordinarily prepared is spontaneously inflammable when in contact with air; but this does not occur if the gas be pure. This spontaneous inflammability is due to the presence of the vapor of liquid hydrogen phosphide, H_3P, one part of which in 500 parts of H_3P is sufficient to confer this property upon it.

CHLORINE, Cl.

Atomic weight, 35.5. Atomic volume, 1. Molecular weight, 71. Molecular volume, 2. Valence I. Specific gravity compared with air, 2.47. Specific gravity of chlorine in the liquid state, 1.33. 35.5 grammes measure 11.16 litres.

Special history: Scheele recognized it in 1774, and called it "dephlogisticated muriatic acid." In 1810 Davy demonstrated its elementary nature, and called it chlorine.

Natural history: It is never found free in nature. It occurs in combination with sodium and with other metals in salt mines, sea water, and in various minerals as argentic chloride, plumbic chloride, etc. In volcanic districts it is found in combination with hydrogen as vapor of hydrochloric acid.

It is present, in combination, in all foods, especially in those of animal origin, and is a constituent of all animal secretions.

Preparation: 1. By heating manganese dioxide with hydrochloric acid.

$$\overset{\text{Manganese Dioxide.}}{MnO_2} + \overset{\text{Hydrochloric Acid.}}{4HCl} = \overset{\text{Manganous Chloride.}}{MnCl_2} + \overset{\text{Water.}}{2H_2O} + \overset{\text{Chlorine.}}{Cl_2}.$$

2. By heating a mixture of sodium chloride and manganese dioxide with sulphuric acid.

$$\overset{\text{Sodium Chloride.}}{2NaCl} + \overset{\text{Manganese Dioxide.}}{MnO_2} + \overset{\text{Sulphuric Acid.}}{2H_2SO_4} = \overset{\text{Manganese Sulphate.}}{MnSO_4} + \overset{\text{Sodium Sulphate.}}{Na_2SO_4} + \overset{\text{Water.}}{2H_2O} + \overset{\text{Chlorine.}}{Cl_2}.$$

If sodium chloride alone, without manganese dioxide, be heated with sulphuric acid, hydrochloric acid gas will be given off. Thus:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

3. By heating calcium hypochlorite (bleaching lime) with sulphuric acid.

$$CaCl_2O + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

CHLORINE AND HYDROGEN.

HYDROCHLORIC ACID, HCl.

Molecular weight, 36.5. Molecular volume, 2. Specific gravity compared with hydrogen, 18.25. 36.5 grammes measure 22.32 litres.

Special history: It was first obtained, in its gaseous form, by Priestley in 1772. Scheele suspected its real nature in 1774, but it was believed by others to be an element. Davy finally established its true composition.

Natural history: Hydrochloric acid is not found in the free state in the animal kingdom, except in the gastric juice. It is also not found free in the vegetable kingdom. It is a constituent of the gases issuing from volcanoes. The white clouds hovering over the crater of an active volcano are largely due to gaseous hydrochloric acid entering into combination with aqueous vapor in the air to form vapors of the liquid acid.

Preparation: 1. By exposing a mixture of hydrogen and chlorine to sunlight.

$$H + Cl = HCl.$$

2. By heating sodium chloride with sulphuric acid at a moderate temperature.

$$\overset{\text{Sodium Chloride.}}{NaCl} + \overset{\text{Sulphuric Acid.}}{H_2SO_4} = \overset{\text{Acid Sodium Sulphate.}}{NaHSO_4} + \overset{\text{Hydrochloric Acid.}}{HCl.}$$

At a higher temperature the following reaction occurs:

$$\overset{\text{Sodium Chloride.}}{2NaCl} + \overset{\text{Sulphuric Acid.}}{H_2SO_4} = \overset{\text{Normal Sodium Sulphate.}}{Na_2SO_4} + \overset{\text{Hydrochloric Acid.}}{2HCl.}$$

Properties: A colorless gas having a pungent odor and a strong acid taste. It is poisonous to animal and vegetable life. Under a pressure of 40 atmospheres at a temperature of 10° C. (50° F.) it forms a colorless liquid having a specific gravity of 1.27. It is not combustible nor a supporter of combustion.

Hydrochloric acid gas is exceedingly soluble in water, one volume of water absorbing from 480 to 500 times its volume of the gas, forming the ordinary liquid hydrochloric acid of commerce.

HYDROCHLORIC ACID, HCl (Muriatic Acid).

(The Aqueous Solution of the Gas.)

Preparation: 1. By dissolving hydrochloric acid gas in cold water; the water will increase in density and also in volume. The increase in volume of the liquid up to the point of saturation is about $\frac{1}{7}$, *i. e.*, 7 volumes of water increase to 8 volumes. The saturated solution has a specific gravity of 1.21.

A convenient mixture for preparing the gas is composed of

Sodium chloride, ...	6 ounces.
Sulphuric acid, ...	10 "
Water, ...	5 "

The gas produced on heating this mixture is conducted into 7 ounces of cold water until the volume of liquid has increased to 8 ounces. The solution of acid thus prepared is saturated and has a specific gravity of 1.21.

Properties: A colorless liquid when pure, but as found in commerce it is usually slightly yellow. The acid having a specific gravity of 1.11 contains 20 per cent. of anhydrous HCl, that of 1.21 specific gravity contains 42 per cent. of anhydrous HCl.

The ordinary acid sometimes contains impurities, as sulphuric acid, arsenic, iron, tin and lead.

Chemical properties: It is the type of the hydrogen acids.

The hydrogen of the acid may be replaced by a metal forming a simple salt called a chloride.

All chlorides are soluble in water, except argentic chloride, mercurous chloride and plumbic chloride.

The Metals may be divided into three Classes, according to their Behavior with Hydrochloric Acid:

1. Those which decompose the acid at ordinary temperature, as iron, zinc, etc.

2. Those which decompose the acid only on the application of heat, as copper, mercury, etc.

3. Those which have no action on the acid, as the noble tals, gold, platinum, etc.

Hydrochloric acid decomposes nitric acid, with the formation of nitro-hydrochloric acid (aqua regia), which is a solution containing azotyle chloride and free chlorine. Three molecules of hydrochloric acid act upon one molecule of nitric acid, thus:

$$\overset{\text{Hydrochloric Acid.}}{3HCl} + \overset{\text{Nitric Acid.}}{HNO_3} = \overset{\text{Water.}}{2H_2O} + \overset{\text{Azotyle Chloride.}}{NOCl_2} + \overset{\text{Chlorine.}}{Cl.}$$

When nitro-hydrochloric acid is heated, it evolves nitrogen protoxide and chlorine, which latter, in the nascent state, dissolves gold and platinum: thus, in the case of gold:

$$\overset{\text{Azotyle Chloride.}}{2NOCl_2} + \overset{\text{Chlorine.}}{2Cl} + \overset{\text{Gold.}}{2Au} = \overset{\text{Gold Chloride.}}{2AuCl_3} + \overset{\text{Nitrogen Protoxide.}}{N_2O_2.}$$

Selenic acid, H_2SeO_4, is the only single acid that will dissolve gold.

COMPOUNDS OF CHLORINE AND OXYGEN.

Chlorine combines with oxygen in several proportions to form oxides. All the compounds of chlorine and oxygen are unstable. The direct union of chlorine with oxygen has never been effected.

There are possibly five compounds of chlorine and oxygen. Only three of them have thus far been isolated.

Cl_2O,	Hypochlorous oxide or anhydride.	
Cl_2O_3,	Chlorous oxide or anhydride.	
Cl_2O_4,	Chlorine peroxide.	
Cl_2O_5,?	Chloric oxide or anhydride.	Have never been obtained in their uncombined state.
Cl_2O_7,?	Perchloric oxide or anhydride.	

These oxides of chlorine, except chlorine peroxide, enter into combination with the elements of water to form acids, namely:

$Cl_2O + H_2O = 2HClO$, Hypochlorous acid.
$Cl_2O_3 + H_2O = 2HClO_2$, Chlorous acid.
$Cl_2O_5 + H_2O = 2HClO_3$, Chloric acid.
$Cl_2O_7 + H_2O = 2HClO_4$, Perchloric acid.

HYPOCHLOROUS ANHYDRIDE, Cl_2O.

Molecular weight, 87. Molecular volume, 2. Specific gravity compared with hydrogen, 43.5; with air, 3.01.

Preparation: By passing dry chlorine over dry mercuric oxide.

$$\overset{\text{Mercuric Oxide.}}{2HgO} + \overset{\text{Chlorine.}}{Cl_4} = \overset{\text{Mercuric Oxychloride.}}{HgCl_2,HgO} + \overset{\text{Hypochlorous Oxide.}}{Cl_2O.}$$

Properties: A deep yellowish-green gas, having an intensely suffocating odor. At a temperature of —20° C. (—4° F.) it is condensed to a red liquid. On exposing the liquid to direct sunlight, or applying a slight heat, it undergoes decomposition with explosive violence.

With the elements of water it forms hypochlorous acid, $HClO$.

HYPOCHLOROUS ACID, $HClO$.

Preparation: By the action of water on hypochlorous anhydride.

$$Cl_2O + H_2O = 2HClO.$$

Properties: A yellowish-red liquid, having an odor resembling that of chlorine. It is a strong irritant poison.

Hypochlorous acid enters into combination with basic substances, forming unstable salts, called hypochlorites. Sodium or potassium hypochlorite may be prepared by passing chlorine into a solution of, respectively, sodium hydroxide or potassium hydroxide.

$$\overset{\text{Sodium Hydroxide.}}{2NaOH} + \overset{\text{Chlorine.}}{Cl_2} = \overset{\text{Sodium Hypochlorite.}}{NaClO} + \overset{\text{Sodium Chloride.}}{NaCl} + \overset{\text{Water.}}{H_2O.}$$

Calcium hypochlorite is prepared by bringing chlorine in contact with recently slaked lime.

$$2CaO + Cl_4 = \overset{\text{Calcium Hypochlorite.}}{2CaCl_2O.}$$

Calcium hypochlorite is the ordinary chlorinated lime or bleaching lime, largely used for disinfecting and bleaching purposes. Its bleaching action is due to its property of evolving oxygen, which in the nascent state is the real bleaching agent.

The hypochlorites of the alkalies have a strong decomposing action on certain organic substances, as, for example, urea is broken up by their action into carbon dioxide, water and nitrogen.

$$\overset{\text{Urea.}}{CO(NH_2)_2} + \overset{\text{Sodium Hypochlorite.}}{3NaClO} = 3NaCl + CO_2 + 2H_2O + N_2.$$

CHLOROUS ANHYDRIDE, Cl_2O_3.

Preparation: By heating a mixture of potassium chlorate, arsenious oxide and nitric acid.

$$\overset{\text{Potassium Chlorate.}}{2KClO_3} + \overset{\text{Arsenious Oxide.}}{As_2O_3} + 2HNO_3 = 2KNO_3 + \overset{\text{Arsenic Oxide.}}{As_2O_5} + H_2O + Cl_2O_3.$$

Properties: A yellowish-green gas. It combines with the elements of water to form chlorous acid.

CHLOROUS ACID, $HClO_2$.

Preparation: By the action of water on chlorous anhydride.

$$Cl_2O_3 + H_2O = 2HClO_2.$$

Properties: A very unstable compound. It forms salts called chlorites.

CHLORINE PEROXIDE, Cl_2O_4.

Preparation: By the action of sulphuric acid on potassium chlorate.

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + Cl_2O_4.$$

Properties: A greenish-yellow gas having a strong chlorous odor. At a temperature of 60° C. (140° F.) it undergoes decomposition with explosive violence. It forms neither an acid nor salts.

CHLORIC ANHYDRIDE, Cl_2O_5.

Not known except in combination as chloric acid, $HClO_3$, or as a chlorate of a metal.

CHLORIC ACID, $HClO_3$.

Preparation: By the action of chlorine on potassium hydroxide, forming potassium chlorate $KClO_3$, and then decomposing the latter with hydrofluosilicic acid.

(*a*) $6KOH + Cl_6 = 5KCl + KClO_3 + 3H_2O$.

(*b*) $2KClO_3 + H_2SiF_6 = 2HClO_3 + K_2SiF_6$.

Properties: A syrupy liquid having a strong chlorous odor. It breaks up at a temperature of 38° C. (100° F.) into oxygen, chlorine, perchloric acid and water.

It is a monobasic acid and forms salts called chlorates. The chlorates are soluble in water. They are all decomposed by heat, with the formation of a chloride and the evolution of oxygen. A chlorate heated with charcoal explodes with great violence.

PERCHLORIC ANHYDRIDE, Cl_2O_7.

This anhydride is not known in the free state. It is known only in combination as perchloric acid, $HClO_4$, or as a perchlorate of a metal.

BROMINE, Br.

Atomic weight, 80. Valence I. Specific gravity (liquid) compared with water, 297.

Special history: It was discovered by Balard in 1828, in "bittern," the mother liquor remaining after the crystallization of salt from sea water. At the time it was supposed to be a compound of chlorine and iodine, but its elementary nature was soon afterward proved.

Natural history: It never occurs in nature in the free state. It is contained in sea water in combination as magnesium bromide.

Properties: Bromine is a dark brownish-red liquid, evolving brownish-red fumes at ordinary temperature.

It forms hydrobromic acid, HBr, with hydrogen, and in combination with metals forms simple salts called bromides, as potassium bromide, KBr.

With hydrogen and oxygen it forms hypobromous acid, $HBrO$, the hydrogen of which may be replaced by metals, forming hypobromites, as sodium hypobromite, $NaBrO$.

IODINE, I.

Atomic weight, 127. Valence I. Specific gravity of solid iodine compared with water, 4.97.

Special history: It was discovered by Courtois in 1812.

Natural history: It never occurs in nature in the free state. It is found in sea water as calcium iodide, and in sea weeds as an alkaline iodide. It is said to be an invariable constituent of cod-liver oil (0.04 to 0.32 per cent.).

Preparation: It is obtained from the sodium iodide of the ashes of sea weeds by distilling the solution of sodium iodide with manganese dioxide and sulphuric acid.

$$2NaI + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + I_2.$$

The iodine thus obtained is purified by resublimation.

Properties; Iodine is a bluish-black crystallizable solid. It has a characteristic odor and an acrid taste. It vaporizes at ordinary and also at high temperatures unchanged. The color of the vapor is violet.

It forms hydriodic acid, HI, with hydrogen, and in combination with metals forms simple salts, called iodides, as potassium iodide, KI.

With hydrogen and oxygen it forms iodic acid, HIO_3, the hydrogen of which may be replaced by metals, forming iodates, as potassium iodate, KIO_3.

FLUORINE, FI.

Atomic weight, 19. Valence I.

Fluorine is never found free in nature. It is found in combination as calcium fluoride, CaF_2, and as cryolite, sodium aluminium fluoride $(NaF)_6Al_2F_6$. Bone contains about one per cent. of calcium fluoride.

Preparation: By the action of sulphuric acid on a mixture of manganese dioxide and calcium fluoride.

Properties: A gas said to have a yellow color. It combines with every known element except oxygen. It has a powerful corrosive action on glass. Its combination with hydrogen, hydrofluoric acid, HF, is largely used to etch glass.

GENERAL FACTS REGARDING THE METALS.

Physically, a metal is an opaque body, having a metallic lustre, and possessing, for the most part, a good conducting power for heat and electricity.

Chemically, a metal is an element capable of forming a base by its combination with oxygen, and a salt by its combination with an acidulous radical.

In nature the metals are found either in the free state or in combination. Some are widely distributed, while others are found in small quantities only and in few localities.

The metals under ordinary conditions are solid, with the single exception of mercury.

With the exception of gold (yellow) and copper (red), they are all more or less gray or white in color.

The metals vary in specific gravity from lithium, 0.59, the lightest, to osmium, 22.4, the heaviest.

The melting points of the metals vary greatly. Mercury melts at —38.8° C. (—37.9° F.), gallium at 30° C. (86° F.), sodium and potassium between 60° C. and 100° C. (143° F. and 212° F.), iron at between 1500° and 2500° C. (2732° F. and 4462° F.). They vary in hardness, tenacity, malleability, ductility, etc.

Their commercial value varies from iron, worth about 1 to 2 cents per pound, to vanadium, worth about 5000 dollars a pound. Gold is worth about 300 dollars a pound. There are about twenty metals more valuable, commercially, than gold.

The metals are all electro-positive. Arsenic, antimony and tellurium have the feeblest electro-positive properties, cæsium has the strongest.

They are divided, according to their saturating power compared with hydrogen, into monads, diads, triads, tetrads, etc.

They differ in their atomic weights, from lithium, 7, the lowest, to uranium, 240, the highest. The lower the atomic weight of an element the higher is its capacity for heat.

Example: Lithium, atomic weight 7, capacity for heat 0.940. Uranium, atomic weight 240, capacity for heat 0.027.

The metals may be arranged in four classes, viz.:

1. The alkalies, as potassium, sodium, etc.
2. The alkaline earths, as barium, strontium, calcium and magnesium.
3. The earths proper, as aluminium, cerium.
4. The metals proper, as gold, lead, etc.

The metals are, in addition, arranged in groups according to their behavior with group reagents, as those precipitated by hydrochloric acid, those by hydrogen sulphide, etc.

The metals may unite with one another to form compounds, called respectively alloys and amalgams. An amalgam is a combination of mercury with another metal.

It is not yet determined with absolute certainty whether alloys and amalgams are definite chemical compounds or merely mechanical mixtures.

All the metals combine with oxygen to form oxides, which latter may be arranged in three classes, namely, basic oxides, neutral oxides and oxyacid radicals.

A metal may displace the hydrogen of a hydrogen acid, or the hydrogen of an oxyacid, to form, respectively, a simple salt and an oxysalt.

Chemical affinity is modified by conditions such as temperature, the production of a soluble or an insoluble compound, etc.

The positive or negative intensities of elements and compounds modify chemical combination. If, for example, a basic substance, as potassium hydroxide, be mixed with sulphuric acid and nitric acid, the basic substance, potassium, will distribute itself between the two acids according to its relative affinity for them. In a similar manner if sulphuric acid be mixed with dissimilar basic substances, as potassium hydroxide and sodium hydroxide, the acid will distribute itself between the two basic substances according to its relative affinity for them.

Insolubility affects chemical combination, as for example, if sulphuric acid be added to barium hydroxide and potassium hydroxide, all being present in molecular proportions, the acid will first distribute itself between the two basic substances according to its relative affinity for them, but the combination with barium being insoluble, a portion of the barium is removed from the sphere of chemical action, thus reducing the relative proportion between acid and bases. The remaining barium of the barium hydroxide combines with more acid, until finally all the acid which had been added is in combination with the barium and is precipitated as barium sulphate, the potassium hydroxide remaining unchanged.

Again, on adding together two molecules of argentic nitrate, two molecules of hydrocyanic acid and one molecule of sulphuric acid, it would be expected that the silver of the argentic nitrate would combine with the stronger of the two acids, namely, sulphuric acid, without reference to the weaker acid—hydrocyanic acid. Instead, however, a part of the silver combines with the hydrocyanic acid to form insoluble argentic cyanide, which is thus removed from the sphere of chemical action. Another portion of silver combines with the hydrocyanic acid, and this action continues, until finally all the silver is in combination with the weaker acid, and is precipitated as argentic cyanide, the sulphuric acid remaining uncombined with a base.

SOLUBILITIES.

A substance is termed insoluble when more than 100 times its weight of water is required to dissolve it.

Oxides.	All oxides are insoluble in water, except the oxides of the alkalies and the oxides of barium, strontium and calcium.
Chlorides.	All chlorides are soluble except argentic chloride, mercurous chloride and plumbic chloride.
Bromides.	All bromides are soluble except the bromides of silver, lead, bismuth, copper and mercurous and mercuric bromide.
Iodides.	All iodides are soluble except the iodides of silver, lead, copper, bismuth, tin and mercurous and mercuric iodide.
Sulphides.	All sulphides are insoluble except the sulphides of the alkalies and alkaline earths.
Sulphates.	All sulphates are soluble except the sulphates of barium, strontium, calcium, silver, mercury and lead.
Carbonates.	All carbonates are insoluble except the carbonates of the alkalies and the bicarbonates of the alkaline earths.
Phosphates.	All phosphates are insoluble except the phosphates of the alkalies.
Nitrates.	All nitrates are soluble (except cinchonamine nitrate and oxynitrates).
Chlorates.	All chlorates are soluble.
Bromates.	All bromates are soluble except the bromates of silver, lead and mercury.
Iodates.	The iodates of the alkalies are freely soluble, all others sparingly soluble.
Acetates.	All acetates are soluble.
Arsenites.	All arsenites are insoluble except the arsenites of the alkalies.
Arsenates.	All arsenates are insoluble except the arsenates of the alkalies.

TABLE OF THE ELEMENTS, WITH THEIR CHEMICAL SYMBOLS AND THEIR CORRECTED ATOMIC WEIGHTS.

ELEMENTS.	SYMBOL.	ATOMIC WEIGHT.	ELEMENTS.	SYMBOL.	ATOMIC WEIGHT.
Aluminium,	Al	27.0	**Manganese,**	Mn	54.8
Antimony (Stibium),	Sb	119.6	**Mercury (Hydrargyrum),**	Hg	199.8
Arsenic,	As	74.9	**Molybdenum,**	Mo	95.8
Barium,	Ba	136.8	**Nickel,**	Ni	58.6
Beryllium,	Be	9.1	**Niobium,**	Nb	94.
Bismuth,	Bi	207.	**Nitrogen,**	N	14.01
Boron,	B	10.9	**Osmium,**	Os	195.
Bromine,	Br	79.76	**Oxygen,**	O	15.96 (16.0)
Cadmium,	Cd	111.9	**Palladium,**	Pd	106.2
Cæsium,	Cs	132.7	**Phosphorus,**	P	30.96
Calcium,	Ca	39.9	**Platinum,**	Pt	194.5
Carbon,	C	11.97	**Rhodium,**	Rh	104.
Cerium,	Ce	140.	**Rubidium,**	Rb	85.2
Chlorine,	Cl	35.37	**Scandium,**	Sc	44.
Chromium,	Cr	52.4	**Selenium,**	Se	78.9
Cobalt,	Co	58.6	**Silicon,**	Si	28.
Copper,	Cu	63.2	**Silver (Argentum),**	Ag	107.66
Didymium,	Di	142.3	**Sodium (Natrium),**	Na	22.99
Erbium,	Er	166.	**Strontium,**	Sr	87.3
Fluorine,	Fl	19.	**Sulphur,**	S	31.98
Gallium,	Ga	69.8	**Tantalum,**	Ta	182.
Germanium,	Ge	72.28	**Tellurium,**	Te	125.
Gold (Aurum),	Au	196.2	**Thallium,**	Tl	203.6
Hydrogen,	H	1.	**Thorium,**	Th	232.
Indium,	In	113.4	**Tin (Stannum),**	Sn	117.5
Iodine,	I	126.54	**Titanium,**	Ti	48.
Iridium,	Ir	192.5	**Tungsten (Wolfram),**	W	183.6
Iron (Ferrum),	Fe	55.9	**Uranium,**	Ur	239.
Kalium (Potassium),	K	39.03	**Vanadium,**	Vd	51.2
Lanthanum,	La	138.2	**Ytterbium,**	Yb	173.
Lead (Plumbum),	Pb	206.4	**Yttrium,**	Y	89.
Lithium,	Li	7	**Zinc,**	Zn	65.1
Magnesium,	Mg	23.9	**Zirconium,**	Zr	90.

There are 66 elements known at present with certainty. The existence of Thulium, Terbium, Wasium and Vesbium, as elementary forms of matter, is not yet sufficiently established.

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